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## ERRATA.

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Page	Line	
i, 670	2	for "R·N:C(OEt)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> (OAc) <sub>4</sub> " <i>read</i> "R·N:C(OEt)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> Ac <sub>4</sub> "
"	10	" "C <sub>2</sub> H <sub>5</sub> ·N:C(SET)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> (OAc) <sub>4</sub> " <i>read</i> "C <sub>2</sub> H <sub>5</sub> ·N:C(SET)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> Ac <sub>4</sub> "
"	25	" "SO <sub>2</sub> Me·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·N:C(SET)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> (OAc) <sub>4</sub> " <i>read</i> "SO <sub>2</sub> Me·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·N:C(SET)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> Ac <sub>4</sub> "
"	14*	" "C <sub>2</sub> H <sub>7</sub> ·N:C(OEt)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> (OAc) <sub>4</sub> " <i>read</i> "C <sub>2</sub> H <sub>7</sub> ·N:C(OEt)·S·C <sub>6</sub> H <sub>7</sub> O <sub>5</sub> Ac <sub>4</sub> "

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## ERRATA.

## VOL. CV (TRANS., 1914).

Page	Line	
2126	9 for	"Velocity constant for ethylene oxide"
		Velocity constant for propylene oxide.
	read	"Velocity constant for propylene oxide"
		Velocity constant for ethylene oxide.

## VOL. CVI (ABSTR., 1914).

i. 233	24	for "d- or l-bromocamphorsulphonate" insert "silver."
ii. 613	28	for "boxwood" read "beechwood."

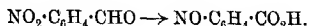
CLXXIX—*Studies in Phototropy and Thermotropy.*  
*Part IV. o-Nitrobenzylidenearylamines and their*  
*Photoisomeric Change.*

By ALFRED SENIER and ROSALIND CLARKE.

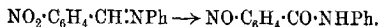
THIS communication is a record of further studies in search of phototropic or thermotropic compounds, and is a continuation of the work contained in previous papers (T., 1909, **95**, 1943; 1911, **99**, 2081; 1912, **101**, 1950). The *o*-nitrobenzylidenearylamines examined were all easily prepared by bringing together the aldehydes and amines in alcoholic solution. All of them are thermotropic, and several exhibit phototropic properties. It is noteworthy, however, that in most cases the prolonged effect of sunlight was to change the bases into non-reversible dimorphic varieties which could be restored generally to the original form by heating to a temperature just below their melting points or by actual melting.

The analogy between the structure of these bases and the *o*-nitro-compounds studied by Ciamician and Silber (*Ber.*, 1901, **34**, 2040) and by Sachs and Kempf (*Ber.*, 1902, **35**, 2704) led us to try if they also would exhibit by prolonged exposure of benzene solutions to sunlight a photoisomeric change with the formation of a nitroso-isomeride. In nearly every instance the photoisomeride was obtained.

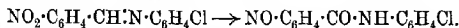
Ciamician and Silber found that *o*-nitrobenzaldehyde changes in benzene solution, giving a precipitate of the less soluble *o*-nitroso-benzoic acid, thus:



Sachs and Kempf in like manner found *o*-nitrobenzylideneaniline to undergo isomeric change with the formation of *o*-nitrosobenzanilide, thus:



Taking as an example the base *o*-nitrobenzylidene-*p*-chloroaniline, we find the isomeric change to be quite analogous, thus:



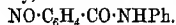
Except in this instance, the quantities obtained were too small to admit of analysis.

The expressions "lower temperature" and "higher temperature" are used throughout in this paper, as in previous communications, to mean respectively the temperature of solid carbon dioxide and a temperature just below the melting point of the substance.

The compounds are all yellow unless otherwise stated, and dissolve in the usual organic solvents from which suitable crystallising media were selected.

*o*-Nitrobenzylideneaniline,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}$ .

This compound, already described by Knoevenagel (*Ber.*, 1898, 31, 2609), exhibits thermotropy at the "lower," but not at the "higher" temperature. It is not phototropic, but under the influence of actinic light it changes into a permanent deeper-coloured *dimorphic variety*, with a melting point  $2^\circ$  lower than that of the original compound. Sachs and Kempf (*loc. cit.*) found that, when exposed to sunlight in benzene solution, it changes into an isomeric nitroso-compound, namely, *o*-nitrosobenzanilide,



*o*-Nitrobenzylidenetoluidines,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ .

*o*-Nitrobenzylidene-*o*-toluidine.—Jaeger (*Chem. Zentr.*, 1906, ii, 325) prepared this compound, and found it to melt at  $96^\circ$ . The specimen examined melted at  $81\text{--}81.5^\circ$  (corr.).

Like its homologous aniline derivative, this compound is thermotropic at the "lower," but not at the "higher" temperature. It is not phototropic, but, when subjected to sunlight, changes to a reddish-brown *dimorphic variety*, the melting point of which is  $4^\circ$  lower than that of the original substance. A benzene solution when exposed to sunlight for some time deepened in colour from yellow to brown, and a precipitate gradually deposited which, after washing with alcohol became colourless. This precipitate is undoubtedly *o*-nitrosobenzo-*o*-toluidide,  $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , analogous to the corresponding aniline compound of Sachs and Kempf. When heated to  $140^\circ$  it decomposes.

As the melting point of the substance prepared differed considerably from that given by Jaeger, an analysis was made:

0.2283 gave 23.1 c.c.  $\text{N}_2$  (moist) at  $13^\circ$  and 741 mm.  $\text{N} = 11.69$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{N} = 11.67$  per cent.

*o*-Nitrobenzylidene-*m*-toluidine melts at  $52\text{--}53^\circ$  (corr.):

0.2459 gave 24.8 c.c.  $\text{N}_2$  (moist) at  $11^\circ$  and 740 mm.  $\text{N} = 11.66$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{N} = 11.67$  per cent.

It is thermotropic at the "lower" temperature, becoming almost colourless, but is not phototropic. The deep red *dimorphic variety* melts  $3^\circ$  below the melting point of the original base. After exposure to sunlight for several weeks a 20 per cent. benzene solution of the base changes to a deep red colour, but only traces of

a precipitate appeared. The solution probably contained the isomeric *o*-nitrosobenzo-*m*-toluidide.

*o*-Nitrobenzylidene-*p*-toluidine melts at 73—74° (corr.):

0.2028 gave 20.7 c.c. N<sub>2</sub> (moist) at 12.5° and 744 mm. N=11.78.

C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires N=11.67 per cent.

It is thermotropic at the "lower," but not at the "higher" temperature, and is not phototropic. The *dimorphic variety* is deep brown, and the melting point is 1—2° lower than that of the original substance. The corresponding *o*-nitrosobenzo-*p*-toluidide is deposited on exposing a benzene solution of the original substance to sunlight for several weeks. It decomposes at 160°.

*o*-Nitrobenzylidenechloroanilines, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH·N·C<sub>6</sub>H<sub>4</sub>Cl.

*o*-Nitrobenzylidene-*o*-chloroaniline melts at 116.5° (corr.):

0.1488 gave 14.3 c.c. N<sub>2</sub> (moist) at 11° and 732.9 mm. N=10.99.

C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Cl requires N=10.75 per cent.

This base exhibits thermotropy both at the "lower" and at the "higher" temperatures, and is slightly phototropic. The *dimorphic variety* is brick-red, and melts 2° below the melting point of the original base. When melted, this dimorphic variety returns to the colour of the original compound, and becomes sensitive to light again. No evidence of the formation of a nitroso-isomeride was obtained.

*o*-Nitrobenzylidene-*m*-chloroaniline separates from solutions in alcohol or light petroleum in cream-coloured needles melting at 77—78° (corr.):

0.1300 gave 12.3 c.c. N<sub>2</sub> (moist) at 11° and 745.7 mm. N=11.01.

C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Cl requires N=10.75 per cent.

This compound exhibits thermotropy at the "lower," but not at the "higher" temperature, and is slightly phototropic. The deep brick-red *dimorphic variety* melts 1° below the melting point of the original base, and on re-solidifying has the same colour as that substance, and behaves in the same manner in the presence of sunlight. The isomeric *o*-nitrosobenzo-*m*-chloroanilide is a powder, which melts and decomposes above 145°.

*o*-Nitrobenzylidene-*p*-chloroaniline melts at 92.5° (corr.):

0.1172 gave 10.7 c.c. N<sub>2</sub> (moist) at 11° and 772 mm. N=11.01.

C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Cl requires N=10.75 per cent.

It is thermotropic both at the "higher" and "lower" temperatures, but is not phototropic. The pale brown *dimorphic variety* has a melting point 2° lower than that of the original compound. Fusion appears to change the dimorphic variety into the original base.

The isomeric *o*-nitrosobenzo-*p*-chloroanilide was obtained by exposing to sunlight an 8 per cent. solution of the original base in benzene. It separated as a yellow powder, from which the colour was removed by washing with warm benzene. It decomposes above  $170^{\circ}$ :

0.1025 gave 9.5 c.c.  $N_2$  (moist) at  $9^{\circ}$  and 766.4 mm.  $N = 11.19$ .

$C_{13}H_9O_2N_2Cl$  requires  $N = 10.75$  per cent.

*o*-Nitrobenzylidenebromoanilines,  $NO_2 \cdot C_6H_4 \cdot CH:N \cdot C_6H_4Br$ .

*o*-Nitrobenzylidene-*o*-bromoaniline forms lemon-yellow needles melting at  $118.5-119^{\circ}$  (corr.):

0.1194 gave 9.3 c.c.  $N_2$  (moist) at  $12^{\circ}$  and 772 mm.  $N = 9.35$ .

$C_{13}H_9O_2N_2Br$  requires  $N = 9.18$  per cent.

It is not phototropic, but exhibits thermotropy at the "lower" temperature. The *dimorphic variety* is brick-red, and melts  $4^{\circ}$  below the melting point of the original substance. Below its melting point it changes back to the original base. All attempts to obtain a nitroso-derivative were unsuccessful.

*o*-Nitrobenzylidene-*m*-bromoaniline melts at  $77-78^{\circ}$  (corr.):

0.1663 gave 13.1 c.c.  $N_2$  (moist) at  $8^{\circ}$  and 762.3 mm.  $N = 9.49$ .

$C_{13}H_9O_2N_2Br$  requires  $N = 9.18$  per cent.

This compound is thermotropic only at the "lower" temperature, and exhibits phototropy at the ordinary temperature when exposed for a minute or two to the action of sunlight. The light brown *dimorphic variety*, which appears to return to the original substance on fusion, has a melting point  $1^{\circ}$  lower than, and not so sharp as, that of the original substance. The isomeric *o*-nitrosobenzo-*m*-bromoanilide decomposes at about  $140^{\circ}$ .

*o*-Nitrobenzylidene-*p*-bromoaniline consists of large, yellow prisms, which melt at  $99^{\circ}$  (corr.):

0.1470 gave 11.8 c.c.  $N_2$  (moist) at  $9^{\circ}$  and 760 mm.  $N = 9.60$ .

$C_{13}H_9O_2N_2Br$  requires  $N = 9.18$  per cent.

This base is thermotropic at the "lower" temperature, but gives only slight indications of thermotropy at the "higher" temperature. It is not phototropic. The deeper-coloured *dimorphic variety* melts at the same temperature as the original substance. The isomeric *o*-nitrosobenzo-*p*-bromoanilide has no well-defined melting point, but decomposes above  $170^{\circ}$ .

*o*-Nitrobenzylideneaminophenols,  $NO_2 \cdot C_6H_4 \cdot CH:NC_6H_4 \cdot OH$ .

*o*-Nitrobenzylidene-*o*-aminophenol consists of long, yellow needles, which melt at  $107.5^{\circ}$  (corr.):

0.1376 gave 14 c.c.  $N_2$  (moist) at  $14^\circ$  and 755.4 mm.  $N=11.84$ .

$C_{18}H_{10}O_3N_2$  requires  $N=11.57$  per cent.

This compound is thermotropic at the "lower" temperature, but not at the "higher" temperature, and is not phototropic. The deep brown *dimorphic variety* melts  $2^\circ$  below the melting point of the original compound, and the colour returns nearly to that of that substance. The isomeric *o-nitrosobenzo-p-hydroxyanilide* does not melt below  $200^\circ$ .

*o-Nitrobenzylidene-m-aminophenol* crystallises in long, yellow prisms, melting at  $106.5-107.5^\circ$  (corr.):

0.1059 gave 10.4 c.c.  $N_2$  (moist) at  $16^\circ$  and 765 mm.  $N=11.44$ .

$C_{18}H_{10}O_3N_2$  requires  $N=11.57$  per cent.

This base is thermotropic at the "lower," but not at the "higher" temperature, and is not phototropic. The *dimorphic variety* melts  $2^\circ$  lower than the melting point of the original base. A small quantity of *o-nitrosobenzo-m-hydroxyanilide* was obtained, which does not melt below  $200^\circ$ .

*o-Nitrobenzylidene-p-aminophenol* was previously obtained by Pope and Fleming (T., 1908, 93, 1918), who found its melting point to be  $159^\circ$ . The specimen examined melted at  $163^\circ$  (corr.). It is thermotropic at both the "lower" and "higher" temperatures, only slightly noticeable at the "lower" temperature. It is not phototropic, the colour remaining unchanged even on prolonged exposure to sunlight or when exposed, surrounded by solid carbon dioxide, to the rays of the mercury lamp. The isomeric *o-nitrosobenzo-p-hydroxyanilide* was obtained; this decomposed when heated to a temperature above the melting point of the original substance.

*o-Nitrobenzylidene-anisidines*,  $NO_2 \cdot C_6H_4 \cdot CH:N \cdot C_6H_4 \cdot OMe$ .

*o-Nitrobenzylidene-o-anisidine* melts at  $64.5-65^\circ$  (corr.):

0.1578 gave 14.6 c.c.  $N_2$  (moist) at  $14^\circ$  and 766.5 mm.  $N=10.93$ .

$C_{14}H_{12}O_3N_2$  requires  $N=10.93$  per cent.

It is thermotropic at the "lower" temperature, but is not phototropic. It gave a brown *dimorphic variety*, which melts at the same temperature as the original compound, and on melting returned to the original base. After seven weeks' exposure to sunlight in benzene solution, the solution became deeper in colour, but no precipitate of a nitroso-isomeride was obtained.

*o-Nitrobenzylidene-m-anisidine* melts at  $74-75^\circ$  (corr.):

0.1571 gave 15.1 c.c.  $N_2$  (moist) at  $16^\circ$  and 759 mm.  $N=11.13$ .

$C_{14}H_{12}O_3N_2$  requires  $N=10.93$  per cent.

It is thermotropic at the "lower" temperature, but is not phototropic. The red *dimorphic variety* has a melting point  $2^\circ$  lower



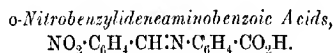
than that of the original substance. When exposed to light in benzene solution, the solution became deeper in colour, but only traces of a nitroso-compound were precipitated.

*o*-Nitrobenzylidene-*p*-anisidine melts at 80–81° (corr.):

0.2761 gave 26.7 c.c. N<sub>2</sub> (moist) at 15° and 756 mm. N=11.21.

C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub> requires N=10.93 per cent.

It shows faint indications of thermotropy at the "higher" temperature, and is distinctly thermotropic at the "lower" temperature, but is not phototropic. The deep brown *dimorphic variety* begins to melt 1–2° below the melting point of the original compound. By fusion the *dimorphic variety* changed back to the original base. Only traces of a *nitroso-isomeride* precipitated, which melted just below 200°.



*o*-Nitrobenzylidene-*o*-aminobenzoic acid has already been described by Pawlewski (*Ber.*, 1904, **37**, 595), who found it to melt at 170–171°, or after a second recrystallisation from alcohol at 167–168°. The specimen prepared was recrystallised from xylene, and was found to melt at 176° (corr.).

*o*-Nitrobenzylidene-*o*-aminobenzoic acid is thermotropic at the "lower" temperature, but is not phototropic. After three weeks' exposure to sunlight at the ordinary temperature, a *dimorphic variety* was obtained, the melting point of which was 1–2° lower than that of the original compound. It did not change apparently on fusion. Only minute traces of a *nitroso-isomeride* were obtained.

*o*-Nitrobenzylidene-*m*-aminobenzoic acid crystallises from acetone in pale yellow needles. It dissolves in alcohol or chloroform, only very sparingly in benzene or ether, and is insoluble in light petroleum. It melts and decomposes at 225° (corr.):

0.1266 gave 11.4 c.c. N<sub>2</sub> (moist) at 14° and 764.2 mm. N=10.60.

C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub> requires N=10.37 per cent.

*o*-Nitrobenzylidene-*m*-aminobenzoic acid is slightly thermotropic at the "lower" temperature. It is not phototropic. The brick-red *dimorphic variety* on heating to 110° apparently changes back to the original base. No *nitroso-isomeride* was obtained.

*o*-Nitrobenzylidene-*p*-aminobenzoic acid crystallises from alcohol or acetone in small, yellow prisms. It dissolves sparingly in chloroform, still less in ether, and is insoluble in benzene or light petroleum. It has no distinct melting point, but decomposes above 230°:

0.2302 gave 20.2 c.c.  $N_2$  (moist) at  $13^\circ$  and 758 mm.  $N=10.29$ .

$C_{14}H_{10}O_4N_2$  requires  $N=10.37$  per cent.

*o*-Nitrobenzylidene-*p*-aminobenzoic acid is thermotropic at both "lower" and "higher" temperatures. It is not phototropic. The yellowish-green *dimorphic variety* melts and decomposes below  $230^\circ$ , the temperature at which the original compound decomposes. The substance does not dissolve in benzene, and no nitroso-compound was obtained.

*o*-Nitrobenzylidenexylidines,  $NO_2 \cdot C_6H_4 \cdot CH \cdot N \cdot C_6H_5Me_2$ .

*o*-Nitrobenzylidene-*o*-4-xylidine melts at  $85^\circ$  (corr.):

0.2300 gave 22.1 c.c.  $N_2$  (moist) at  $17^\circ$  and 763 mm.  $N=11.15$ .

$C_{15}H_{14}O_2N_2$  requires  $N=11.03$  per cent.

This base is thermotropic at the "lower" temperature, but shows no indication of phototropy. The yellowish-brown *dimorphic variety* returns to the colour of the original base on fusion. The isomeric *o*-nitrosobenzo-*o*-4-xylidide obtained melts and decomposes at about  $170^\circ$ .

*o*-Nitrobenzylidene-*m*-4-xylidine melts at  $83^\circ$  (corr.):

0.2492 gave 24.4 c.c.  $N_2$  (moist) at  $14^\circ$  and 738 mm.  $N=11.13$ .

$C_{15}H_{14}O_2N_2$  requires  $N=11.03$  per cent.

It is thermotropic at the "lower" temperature. When exposed to sunlight until a slight change of colour takes place the substance is phototropic. The *dimorphic variety* melts  $1-2^\circ$  lower than the melting point of the original substance, and not so sharply as the latter. The isomeric *o*-nitrosobenzo-*m*-4-xylidide decomposes at about  $150^\circ$ .

*o*-Nitrobenzylidene-*p*-xylidine melts at  $75^\circ$  (corr.):

0.2416 gave 23.3 c.c.  $N_2$  (moist) at  $14^\circ$  and 740 mm.  $N=10.99$ .

$C_{15}H_{14}O_2N_2$  requires  $N=11.03$  per cent.

*o*-Nitrobenzylidene-*p*-xylidine shows faint indications of thermotropy at both the "lower" and "higher" temperatures, but is not phototropic. The deeper-coloured *dimorphic variety* melts  $6^\circ$  below the melting point of the original base. Traces of *o*-nitrosobenzo-*p*-xylidide, which melts and decomposes at about  $125^\circ$ , were obtained.

*o*-Nitrobenzylidenenaphthylamines,  $NO_2 \cdot C_6H_4 \cdot CH \cdot N \cdot C_{10}H_7$ .

*o*-Nitrobenzylidene- $\alpha$ -naphthylamine melts at  $118-118.5^\circ$  (corr.):

0.2478 gave 21.3 c.c.  $N_2$  (moist) at  $14^\circ$  and 766.8 mm.  $N=10.16$ .

$C_{17}H_{12}O_2N_2$  requires  $N=10.14$  per cent.

This base is thermotropic at the "lower" and "higher" temperatures, but is not phototropic. The *dimorphic variety* is deeper

in colour than the original compound, but the melting point is the same. No nitroso-compound was obtained.

*o*-Nitrobenzylidene- $\beta$ -naphthylamine, already prepared by Haase (*Ber.*, 1903, **36**, 594), is stated by him to melt at  $91^{\circ}$ . When crystallised from light petroleum the specimen we examined melted at  $95$ – $96^{\circ}$  (corr.). It is thermotropic at the "lower" temperature, and is slightly thermotropic at the "higher" temperature, but it is not phototropic. The deep brown *dimorphic variety* begins to melt  $5^{\circ}$  below the melting point of the original substance. No nitroso-compound was obtained, although the colour of the benzene solution by exposure to sunlight changed from yellow to very deep brown.

*o*-Nitrobenzylidene- $\psi$ -cumidine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Me}_3$ , melts at  $112.5$ – $113.5^{\circ}$  (corr.):

0.2081 gave 18.6 c.c.  $\text{N}_2$  (moist) at  $12^{\circ}$  and 755 mm.  $\text{N} = 10.49$ .

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{N} = 10.45$  per cent.

It is thermotropic at both the "lower" and "higher" temperatures, but is not phototropic. The yellowish-brown *dimorphic variety* melts  $1$ – $2^{\circ}$  below the melting point of the original substance. No nitroso-isomeride was obtained.

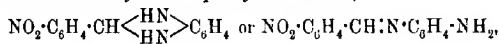
*Di-o-nitrobenzylidenebenzidine*,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_2 : (\text{N} \cdot \text{C}_6\text{H}_4)_2$ .—This compound is obtained when *o*-nitrobenzaldehyde (2 mols.) reacts with benzidine (1 mol.) in alcoholic solution. It crystallises from chloroform in yellow prisms. It dissolves in benzene, sparingly in alcohol, more sparingly in acetone, and is nearly insoluble in light petroleum. It melts at  $231.5$ – $232.5^{\circ}$  (corr.):

0.1542 gave 16.8 c.c.  $\text{N}_2$  (moist) at  $16^{\circ}$  and 756 mm.  $\text{N} = 12.57$ .

$\text{C}_{26}\text{H}_{18}\text{O}_4\text{N}_4$  requires  $\text{N} = 12.44$  per cent.

This base is thermotropic at the "higher" temperature, and only faintly thermotropic at the "lower" temperature. It is not phototropic. The deep yellow *dimorphic variety* melts at a lower temperature than does the original base. No nitroso-isomeride separated on exposing the benzene solution to sunlight.

*Mono-o-nitrobenzylidene o-phenylenediamine*,



is obtained when *o*-phenylenediamine (1 mol.) is treated with *o*-nitrobenzaldehyde (1 or 2 molecular proportions) in alcoholic solution. The di-derivative was not obtained. It crystallises from alcohol or light petroleum in red needles, melting at  $93$ – $94^{\circ}$  (corr.):

0.1455 gave 21.9 c.c.  $\text{N}_2$  (moist) at  $16^{\circ}$  and 757 mm.  $\text{N} = 17.39$ .

$\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3$  requires  $\text{N} = 17.42$  per cent.

*Mono-o-nitrobenzylidene-o-phenylenediamine* is thermotropic both

at the "lower" and "higher" temperature. It is not affected by sunlight at the ordinary temperature, nor when exposed to rays from the mercury lamp at the temperature of solid carbon dioxide. *Mono-o-nitrosobenzo-o-phenylenediamide* was obtained as a light-coloured powder with a melting point above  $210^{\circ}$ .

*Di-o-nitrobenzylidenephenylenediamines,*  
 $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4$ .

*Di-o-nitrobenzylidene-m-phenylenediamine*, prepared from *m*-phenylenediamine (1 mol.) and *o*-nitrobenzaldehyde (2 mols.), crystallises from acetone in small, lemon-yellow needles, which dissolve in alcohol, benzene, or chloroform, sparingly in ether, and very sparingly in light petroleum. It melts at  $141.5^{\circ}$  (corr.):

0.1052 gave 13.5 c.c.  $\text{N}_2$  (moist) at  $15^{\circ}$  and 764.3 mm.  $\text{N} = 15.04$ .

$\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_4$  requires  $\text{N} = 14.97$  per cent.

*Di-o-nitrobenzylidene-m-phenylenediamine* is slightly thermotropic both at the "lower" and "higher" temperature. It is not phototropic. The *dimorphic variety* obtained by exposure to sunlight is brownish-yellow, and its melting point is  $1-2^{\circ}$  below that of the original compound. The yellow benzene solution became dark red after some weeks' exposure to light, and traces of a precipitate of *di-o-nitrosobenzo-m-phenylenediamide* melting above  $200^{\circ}$  were obtained.

*Di-o-nitrobenzylidene-p-phenylenediamine* crystallises from alcohol and other solvents in deep yellow needles, melting at  $214.5^{\circ}$  (corr.). It dissolves in chloroform, but is almost insoluble in ether:

0.1150 gave 14.5 c.c.  $\text{N}_2$  (moist) at  $16^{\circ}$  and 775.3 mm.  $\text{N} = 14.93$ .

$\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_4$  requires  $\text{N} = 14.97$  per cent.

*Di-o-nitrobenzylidene-p-phenylenediamine* is thermotropic at both the "lower" and "higher" temperatures, but is not phototropic. The greenish-brown *dimorphic variety* on heating to  $150^{\circ}$  returns to the colour of the original compound. At a higher temperature the *dimorphic variety* deepens again in colour, and melts and decomposes about  $5^{\circ}$  below the melting point of the original substance. After exposing a benzene solution for eight weeks to sunlight, the colour changed very little, and only traces of a precipitate of a *nitroso-compound* were deposited.

CLXXX.—*Calcium Nitrate. Part III. The Three-component System: Calcium Nitrate-Lime-Water.*

By HENRY BASSETT, jun., and HUGH STOTT TAYLOR.

HAVING studied the equilibrium between calcium nitrate and water and calcium nitrate and water plus nitric acid (Bassett and Taylor, T., 1912, 101, 576), it was necessary, in order to complete the investigation of the system  $\text{CaO}-\text{N}_2\text{O}_5-\text{H}_2\text{O}$ , to study the equilibria in alkaline solutions.

We were anxious to carry out this investigation partly because of the considerable interest attaching to the so-called "basic salts," which in the case of basic calcium nitrate is increased owing to the use which has been made of it technically, and partly to test the results obtained in a similar investigation by Cameron and Robinson (*J. physical Chem.*, 1907, 11, 273). According to these observers,  $\text{Ca}(\text{OH})_2$ ; a solid solution,  $\text{CaO}, x\text{N}_2\text{O}_5, y\text{H}_2\text{O}$ ; the basic nitrate,  $2\text{CaO}, \text{N}_2\text{O}_5, 3\frac{1}{2}\text{H}_2\text{O}$ ; and  $\text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}$  could be in stable equilibrium with alkaline solutions of calcium nitrate at  $25^\circ$ .

It seemed very unlikely to us that a powerful base like lime should give rise to any such indefinite solid solution with such a strong acid as nitric acid, and our experiments have fully borne out this view. The portion of Cameron and Robinson's  $25^\circ$  isothermal, in which the solid phase in equilibrium is regarded as a solid solution, is in reality a part of the curve corresponding with  $\text{Ca}(\text{OH})_2$  as equilibrium solid. With regard to the crystalline basic nitrate the compound stable at  $25^\circ$  has the formula  $\text{Ca}_2\text{N}_2\text{O}_7, 3\text{H}_2\text{O}$ , and not  $\text{Ca}_2\text{N}_2\text{O}_7, 3\frac{1}{2}\text{H}_2\text{O}$ , as has been hitherto assumed. At  $100^\circ$  the hydrates  $\text{Ca}_2\text{N}_2\text{O}_7, 2\text{H}_2\text{O}$  and  $\text{Ca}_2\text{N}_2\text{O}_7, \frac{1}{2}\text{H}_2\text{O}$  may exist in equilibrium with the solutions. The experiments at this temperature, moreover, afford additional proof of the non-existence of the solid solution. As will be shown presently, the presence of a small amount of magnesia in the calcium nitrate employed by Cameron and Robinson may possibly have caused complications which led them to erroneous conclusions.

We have found no indications of any other basic salt intermediate between  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}_2\text{N}_2\text{O}_7$ .

## EXPERIMENTAL.

Since even weakly alkaline solutions exert a marked solvent action on glass, and since a considerable time was required for equilibrium conditions to be attained at  $25^\circ$ , it seemed very undesirable to employ glass bottles for the experiments. We therefore used

narrow-mouthed bottles of cerasin wax, of approximately 100 c.c. capacity. These were found eminently satisfactory. They were closed with stoppers of cerasin wax, which were made liquid-tight by running melted wax round the junction of bottle and stopper.

These bottles were rotated in a thermostat kept at 25° for periods of upwards of six months, which was considerably longer than the time actually required for equilibrium to be reached.

When ready for analysis the contents of the bottles were allowed to settle, and some of the clear solution withdrawn, weighed, and analysed. The solid phase was filtered off in the thermostat (Bassett, *Zeitsch. anorg. Chem.*, 1908, **59**, 12), and the moist solid weighed and analysed.

The method of analysis adopted was to titrate the free lime with  $N/10$ -nitric acid in the presence of methyl-orange, and then to determine the total lime in the titrated solution by weighing as calcium oxide after precipitation as oxalate. The percentage of  $N_2O_5$  present was then calculated from the two results.\* In titrating the free lime, care had to be taken in cases where there was a large amount of calcium nitrate and a small amount of free lime present, to dilute the solution considerably in order to obtain a sharp end-point. It seems probable that this is due to a neutral-salt effect on the methyl-orange employed as indicator, as discussed by Thiele (Ahrens' "Sammlung," 1911, **16**, 307). Difficulties due to hydrolysis of the normal salt were not observed.

Merck's calcium nitrate was used in the experiments described in this paper, whilst the additional lime required was obtained by the ignition of pure calcium carbonate precipitated from solutions by means of ammonium carbonate.

Although analyses seemed to show that the materials employed were satisfactorily pure, we were surprised to find from analyses of the moist equilibrium solids that these frequently contained a small amount of magnesia. This was traced to the calcium nitrate. By a slight modification of Herzfeld and Förster's method (*Zeitsch. Verein Rubenzucker-Ind.*, 1896, 284) it was found that the sample of Merck's calcium nitrate used for the experiments at 100° contained 0.017 per cent. of magnesia, the amount of calcium nitrate being 77 per cent. The material employed for the experiments at 25° must have contained still less, as the solutions were made up from tetrahydrate which had been at least once recrystallised.

Now although this amount of magnesia is so small that it cannot be detected in the ordinary way, and would not cause any trouble

\* This method was also used by Cameron and Robinson, but in their experiments the indicator used was phenolphthalein.

in neutral or acid solutions, yet in the present series of experiments, in which the solutions are alkaline, all the magnesia accumulates in the solid phase, being displaced from combination by the stronger base, lime. As, moreover, the amount of solid is comparatively small, there is a possibility of a relatively considerable percentage of magnesia being thus introduced into the equilibrium solid.

From the method of analysis adopted in the present work it is obvious that the magnesia present would be titrated by the acid and reckoned as lime, whereas it would be ignored in the estimation of the total lime. Consequently, the amount of  $N_2O_5$  in the moist solid found by calculation would be too low, and the resulting diagrammatic representation of the values obtained would lead to erroneous conclusions. Thus, in the case of a crystalline basic salt the effect would be to cause a higher hydration value to be ascribed to the salt in question, whilst a series of solid solutions might be indicated, where in reality the solid phase was the hydroxide.

There can be little doubt that one of the chief difficulties to be anticipated in the investigation of basic salts is contamination of the solid phase either through the solvent action of the solution, which will often be alkaline, on solubility vessels of unsuitable material, or through the displacement of traces of less basic oxides from the solutions, as in the case just discussed. The great length of time required for the attainment of equilibrium renders the former source of contamination all the more serious. It seems to us that the importance of these two disturbing factors has hitherto not been duly appreciated in phase-law investigations.

For the experiments at  $100^\circ$  a long-necked platinum flask of 100 c.c. capacity was employed. By means of a suitable shaking arrangement the contents of the flask were maintained in a state of agitation. The flask was closed by a well-fitting cork, the neck of the flask projecting several cm. from the suitably regulated oil-bath employed as thermostat. This thermostat was of 9 litres capacity, and, after trial of several oils, "Mobile oil B" was found to work the most satisfactorily as thermostat liquid.\* Stirring must be vigorous; otherwise, owing to the low specific heat of the oil, local irregularities of temperature may occur. The usual toluene regulator was employed, the temperature variation being  $\pm 0.2^\circ$ . The time required for equilibrium varied with the concentration of solution employed. In the weaker solutions four days were ample, whilst at the higher concentrations as long as ten days to a fortnight were necessary.

\* The oil requires to be renewed after about two months because of the formation of a carbonaceous deposit which interferes with the heating.

In the experiments at  $100^{\circ}$  the traces of magnesia present were removed from the calcium nitrate solutions by preliminary treatment in the platinum flask at  $100^{\circ}$  with excess of pure lime. After twenty-four hours the solutions were filtered in a jacketed filter tube, and the purified solution thus obtained was employed in the experiment. Weak solutions could in this manner be purified directly. The more concentrated solutions were usually obtained by concentrating a 55 per cent. calcium nitrate solution which had been previously purified. The evaporation in the platinum flask took place quite smoothly, and by occasionally weighing the flask and contents a solution of the required concentration could be obtained. The amount of lime necessary for the formation of a suitable amount of equilibrium solid was added to the purified calcium nitrate solution previous to the concentration.

Microscopic examination of the solid phase was always made either before or immediately after filtration from the equilibrium solution.

A few experiments had been carried out at  $100^{\circ}$  with calcium nitrate containing a trace of magnesia before the presence of the latter was discovered. The results of these experiments have been utilised, and are included in table II, since experiments made with magnesia-free nitrate showed that the presence of the magnesia in the solid phase had no measurable effect on the composition of the equilibrium solutions. The composition of the moist solid has been corrected for the trace of magnesia, assuming it all to be present as  $Mg(OH)_2$ . The amount of magnesia present is given. In all other cases purified nitrate had been used, and magnesia was absent.

#### *25° Isothermal.*

The data obtained from the analyses of the various solutions and the moist solids in equilibrium at  $25^{\circ}$  are presented in table I. With the exception of the first three experiments, the analyses of the moist solids have been corrected for the small amounts of magnesia present. In experiments 24, 25, and 26, the solid in equilibrium was not analysed, as the analyses of the solutions showed their close proximity to other solutions the equilibrium solid of which had been shown to be the basic nitrate.

The results obtained from the analyses of the solutions are expressed graphically in Fig. 1. The triangular diagram, Fig. 2, represents the results of the analyses of the solutions and their moist equilibrium solids.

The curves obtained by the study of the system are three in number, and by reference to Fig. 2 may be seen to correspond with the solid phases  $Ca(OH)_2$ ,  $Ca_2N_2O_7 \cdot 3H_2O$ , and  $Ca(NO_3)_2 \cdot 4H_2O$ .



TABLE I.  
25° *Isothermal*.

Experi- ment.	Grams per 100 grams of solution.				Grams per 100 grams of moist solid (corrected for Mg(OH) <sub>2</sub> present).				Nature of the solid phase.
	"Free " CaO.	Total CaO.	Ca(NO <sub>3</sub> ) <sub>2</sub> .	N <sub>2</sub> O <sub>5</sub> .	MgO in original moist solid. Not estimated	"Free "		Total CaO.	
						CaO.	N <sub>2</sub> O <sub>5</sub> .		
*1	0.0978	1.75	4.836	3.18	"	38.97	40.15	2.15	Ca(OH) <sub>2</sub>
*2	0.1074	3.29	9.36	6.16	"	36.30	38.16	3.60	Ca(OH) <sub>2</sub>
3	0.1193	4.83	13.77	9.07	"	43.25	46.56	4.34	Ca(OH) <sub>2</sub>
*4	0.1265	5.59	15.98	10.53	0.01	43.28	45.53	4.33	Ca(OH) <sub>2</sub>
5	0.1342	6.85	19.65	12.95	Trace	33.37	37.49	7.93	Ca(OH) <sub>2</sub>
*6	0.1444	7.82	22.46	14.78	0.20	34.44	39.07	8.93	Ca(OH) <sub>2</sub>
7	0.1624	9.27	26.63	17.35	0.22	43.67	48.18	8.63	Ca(OH) <sub>2</sub>
*8	0.1650	9.675	27.83	18.33	0.13	26.04	32.53	12.51	Ca(OH) <sub>2</sub>
9	0.1755	10.48	30.16	19.87	0.12	27.78	34.59	13.10	Ca(OH) <sub>2</sub>
*10	0.1931	11.45	32.94	21.70	Trace	32.38	38.91	12.58	Ca(OH) <sub>2</sub>
11	0.2093	12.50	35.95	23.59	0.16	40.20	46.50	12.16	Ca(OH) <sub>2</sub>
*12	0.2150	13.02	37.46	24.67	0.10	35.16	42.34	13.81	Ca(OH) <sub>2</sub>
13	0.2460	13.87	39.86	26.25	0.07	44.63	50.41	11.15	Ca(OH) <sub>2</sub>
*14	0.2579	14.15	40.66	26.80	0.34	40.83	48.00	13.77	Ca(OH) <sub>2</sub>

\* Only the results for experiments marked with an asterisk are plotted in Fig. 2.

TABLE 1 (continued).  
 25° Isothermal.

Experi- ment.	Grams per 100 grams of solution.				Grams per 100 grams of moist solid (corrected for $Mg(OH)_2$ present).				Nature of the solid phase.  $Ca(OH)_2$ $Ca(OH)_2$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca_3N_2O_7 \cdot 3H_2O$ $Ca(NO_3)_2 \cdot 4H_2O$
	"Free"		Total		MgO in original moist solid.	"Free"		Total	
	CaO.	$Ca(NO_3)_2$ .	CaO.	$N_2O_5$ .		CaO.	$N_2O_5$ .		
15	0.2722	42.59	14.83	28.06	0.20	38.23	46.03	15.03	
*16	0.3060	44.44	15.50	29.28	0.31	53.61	58.74	9.87	
*17	0.2802	45.28	15.75	29.83	0.01	18.82	39.12	39.10	
18	0.2536	46.80	16.25	30.84	0.055	12.63	31.25	35.86	
*19	0.2314	47.79	16.56	31.49	0.066	9.92	28.53	35.84	
20	0.2158	49.03	16.97	32.30	0.06	11.03	29.85	36.27	
*21	0.1894	51.07	17.64	33.65	0.06	13.39	33.01	37.80	
22	0.1798	51.62	17.82	34.00	0.07	12.53	32.09	37.67	
*23	0.1659	53.20	18.35	35.05	0.02	14.05	33.98	38.41	
†24	0.1647	53.58	18.49	35.29	—	—	—	—	
†25	0.1635	53.79	18.55	35.48	—	—	—	—	
†26	0.1526	54.93	18.93	36.21	—	—	—	—	
*27	0.1486	55.25	19.03	36.40	Trace	13.65	33.82	38.85	
28	0.0836	57.72	19.79	38.01	—	—	—	—	
*29	0.0000	57.98	19.80	38.18	—	—	—	—	

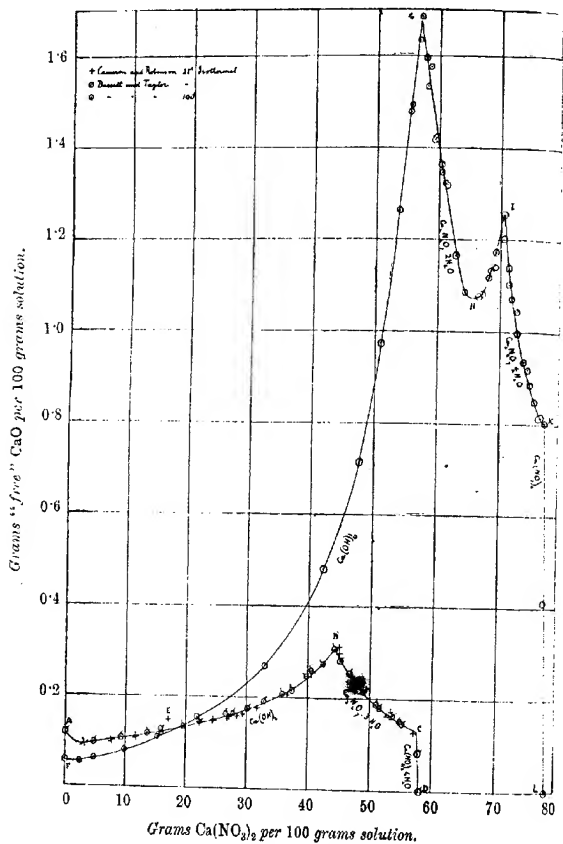
\* Only the results for experiments marked with an asterisk are plotted in Fig. 2.

† These three solids were not analysed.

$\text{Ca}(\text{OH})_2$  Curve AB.

Calcium hydrate can exist in stable equilibrium with solutions containing less than 44.5 grams of calcium nitrate per 100 grams

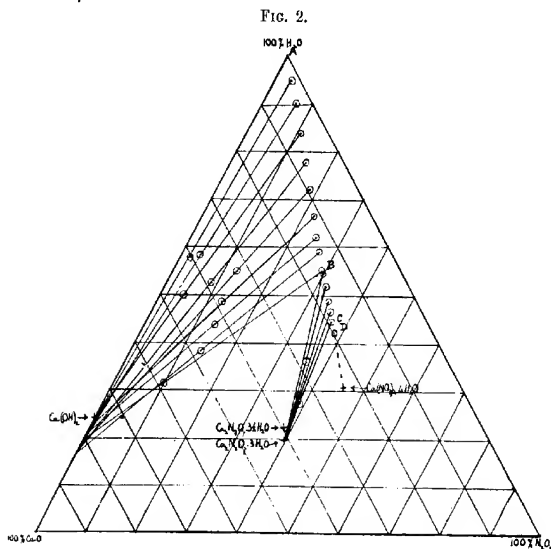
FIG. 1.



of solution. Small quantities of calcium nitrate lower the solubility of lime. In the most concentrated solution the solubility is increased to about three times that in the aqueous solution.

*Basic Nitrate Curve BC.*

Reference to the triangular diagram shows that the equilibrium solids in experiments 17—27 have a composition corresponding with  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ . This basic salt is in stable equilibrium with solutions of calcium nitrate containing from 44.5 to 57.5 grams per 100 grams solution. The solid phase was composed of large,



acicular crystals, many of them at least a centimetre in length owing to the length of time allowed for equilibrium to be attained.

*Tetrahydrate Curve CD.*

The solid phase in equilibrium with solutions along the steep branch of the curve CD was manifestly the normal tetrahydrate.

The figures of Cameron and Robinson have been recalculated to the units, grams per 100 grams solution, and are expressed graphically along with those of the present investigation in Fig. 1. It will be seen that apart from the point E and an uncertainty attaching to their result at point B, their results coincide fairly well with our own. The uncertainty in the latter case arises from the fact that calculation of the Cameron and Robinson values

yields the two different values plotted, according as one calculates from their "grams per 100 c.c." table or from the table "grams per 100 grams water." Possibly an error in the printing may account for this.\* As regards point *B*, it is difficult to suggest how the break in their curve may have been caused, as the curve obtained in the present investigation is quite continuous, and the points corresponding with the results from the seventeen solutions and moist solids when plotted in a triangular diagram give lines all of which converge very closely on the point of composition corresponding with  $\text{Ca}(\text{OH})_2$ . In Fig. 2 only half of these points have been plotted, for the sake of clearness. We consider that our results show that a series of solid solutions, such as is postulated by Cameron and Robinson, does not exist.

The remaining point of divergence between the two series of results is the composition of the basic salt. From Fig. 2 it will be seen that the whole of our points intersect at the point corresponding with the compound  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ . We consider that this evidence is considerably more certain than that previously brought forward, in which the composition is deduced from two single determinations, which may possibly have been contaminated with magnesia, and from the analysis of a compound by Werner (*Ann. Chim. Phys.*, 1892, [vi], 27, 570), which contained some adhering mother liquor. Again, in experiment 17 of the present series it will be seen that analysis of the moist solid showed it to contain a percentage of  $\text{N}_2\text{O}_5$  greater than that in  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , a result impossible if the solid phase were the latter hydrate.

#### 100° Isothermal.

Table II contains the data obtained from the analyses of the various solutions and the moist solids in equilibrium at 100°. The results are represented graphically in Figs. 1 and 3.

When the contents of the platinum flask were ready for analysis they were allowed to settle. From an hour to a day was necessary for this, according to the nature of the solid phase. A suitable amount of clear solution was then removed by means of a warmed pipette, transferred to a weighed flask, cooled and weighed, and then analysed in the manner already described. Some of the solid phase was then removed by filtration through a filter-tube, which passed through an inverted bottle from which the bottom had been removed, and which was filled with water kept at from 98° to 100°. Sometimes a perforated porcelain disk was sufficient to

\* The figure 50.88 in the fourth column of table I in Cameron and Robinson's paper seems undoubtedly to be a misprint for 55.88.

TABLE II.  
100° Isothermal.

Experi- ment.	Grams per 100 grams of solution.				Grams per 100 grams of moist solid.			MgO in original moist solid.	Nature of the solid phases.
	"Free" CaO.	Total CaO.	Ca(NO <sub>3</sub> ) <sub>2</sub> .	N <sub>2</sub> O <sub>5</sub> .	"Free" CaO.	Total CaO.	N <sub>2</sub> O <sub>5</sub> .		
1	0.0561	0.0561	—	—	—	—	—	—	—
*2	0.055	0.882	2.42	1.59	49.08	49.32	0.46	0.13	Ca(OH) <sub>2</sub>
*3	0.0624	1.740	4.91	3.23	40.01	40.87	1.66		Ca(OH) <sub>2</sub>
4	0.081	3.461	9.90	6.52	(not analysed)				Ca(OH) <sub>2</sub>
*5	0.111	5.370	15.39	10.13	35.23	38.45	6.20	0.32	Ca(OH) <sub>2</sub>
*6	0.120	5.623	16.10	10.60	30.45	34.45	7.71	5.77	Ca(OH) <sub>2</sub>
*7	0.155	7.630	21.86	14.38	45.50	49.99	8.65		Ca(OH) <sub>2</sub>
*8	0.269	11.56	33.03	21.74	50.74	55.12	8.44		Ca(OH) <sub>2</sub>
*9	0.480	14.92	42.26	27.82	28.45	38.73	19.80	0.56	Ca(OH) <sub>2</sub>
10	0.713	17.03	47.76	31.44	36.59	(lost)			Ca(OH) <sub>2</sub>
*11	0.973	18.38	50.94	33.53	41.82	49.87	15.51		Ca(OH) <sub>2</sub>
*12	1.261	19.63	53.75	35.38	26.67	38.93	23.94	0.056	Ca(OH) <sub>2</sub>
*13	1.477	20.41	55.40	36.47	15.48	30.68	29.32		Ca(OH) <sub>2</sub>
*14	1.476	20.42	55.43	36.49	31.49	43.53	23.19		Ca(OH) <sub>2</sub>
*15	1.491	20.51	55.65	36.63	20.35	34.85	27.93		Ca(OH) <sub>2</sub> and Ca <sub>3</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O
*16	1.635	21.08	56.89	37.45	19.49	37.70	35.08		Ca(OH) <sub>2</sub> and Ca <sub>3</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O
*17	1.686	21.18	57.03	37.54	14.07	32.88	36.23		Ca <sub>3</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O
18	1.596	21.39	57.91	38.12	(not analysed)				

\* For footnote, see P. 1937.

TABLE II (continued).  
100° Isothermal.

Experi- ment.	Grams per 100 grams of solution.				Grams per 100 grams of moist solid.				Nature of the solid phase.
	"Free," CaO.	Total CaO.	Ca(NO <sub>3</sub> ) <sub>2</sub> .	N <sub>2</sub> O <sub>5</sub> .	"Free," CaO.	Total CaO. (not analysed)	N <sub>2</sub> O <sub>5</sub> .		
19	1.534	21.40	58.16	38.29		34.84	40.76	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
*20	1.576	21.63	58.67	38.62	13.68	35.76	40.43	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
21	1.419	21.69	59.32	39.05	14.77	35.76	40.43	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
22	1.423	21.78	59.58	39.22	15.94	37.50	41.53	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
23	1.420	21.77	59.56	39.21	9.93	31.13	40.83	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
24	1.362	21.98	60.34	39.72	13.54	34.59	40.53	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
*25	1.348	22.00	60.44	39.79	12.64	34.06	41.25	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
26	1.323	22.18	61.06	40.20	14.43	36.03	41.62	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
27	1.320	22.25	61.29	40.36	13.75	35.11	41.20	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
*28	1.167	22.64	62.82	41.35	11.09	32.80	41.82	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
29	1.088	23.08	64.35	42.36	10.63	32.55	42.21	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
*30	1.077	23.77	66.44	43.75	12.11	34.43	43.00	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
31	1.084	23.99	67.10	44.19	9.56	32.16	43.53	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
32	1.120	24.36	68.05	44.82	6.20	29.18	44.32	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
33	1.135	24.57	68.57	45.14		(not analysed)		Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
34	1.174	24.78	69.08	45.47		(not analysed)		Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	
*35	1.141	24.76	69.12	45.50	12.58	35.01	43.20	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O and very little Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	
*36	1.252	25.38	70.60	46.47	13.93	36.78	44.01	Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O and very little Ca <sub>2</sub> N <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	

\* For footnote, see p. 1937.

TABLE II (continued).  
100° Isothermal.

Experi- ment.	Grams per 100 grams of solution.			Grams per 100 grams of moist solid.			Nature of the solid phase.
	"Free" CaO.	Total CaO.	$\text{Ca}(\text{NO}_3)_2$	"Free" CaO.	Total CaO.	$\text{N}_2\text{O}_5$	
*37	1.203	25.28	70.40	13.91	37.80	46.03	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
38	1.140	25.50	71.35	13.16	37.31	46.59	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
*39	1.103	25.51	71.44	13.64	37.99	46.90	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
40	1.071	25.55	71.70	10.49	34.96	47.20	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
41	1.044	25.88	72.70	10.62	41.29	47.52	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
42	0.995	25.86	72.77	12.35	36.87	47.25	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
*43	0.937	26.18	73.85	16.48	40.99	47.23	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
44	0.920	26.41	74.57	15.60	39.85	46.72	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
45	0.886	26.50	74.94	12.55	37.43	47.93	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
*46	0.849	26.73	75.74	15.23	39.80	47.33	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
47	0.814	27.00	76.64	12.42	37.64	48.57	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
48	0.815	27.11	76.94	13.37	38.49	48.38	$\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$
*49	0.804	27.33	77.62	0.499	30.02	56.86	$\text{Ca}(\text{NO}_3)_2$
*50	0.412	26.98	77.74	0.289	28.99	55.26	$\text{Ca}(\text{NO}_3)_2$
*51	0.000		78.43				$\text{Ca}(\text{NO}_3)_2$

\* Only the results of experiments marked with an asterisk are plotted in Fig. 3 to avoid overcrowding. Occasionally it was found impossible to separate any solid phase for analysis owing to its having formed hard lumps. This accounts for the solid not being always analysed.

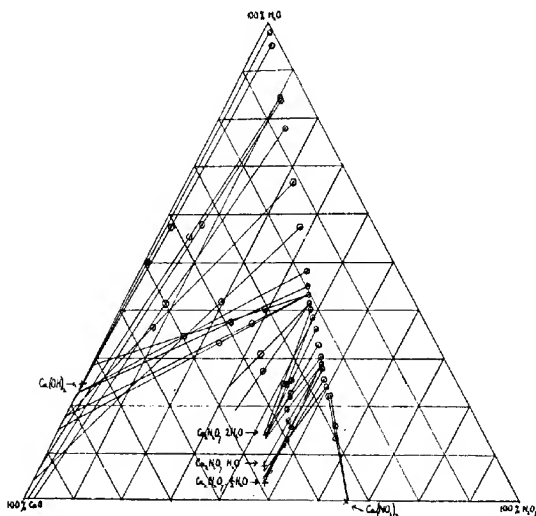
The calcium nitrate used in experiment 6 in the above table contained about 0.2 per cent. of magnesia, which accounts for the large amount of magnesia found in the moist solid. The experiment is included in the table to show that even such a large amount of magnesia does not materially affect the composition of the equilibrium solution.



retain the solid; in other cases a disk of filter paper or even a pad of asbestos had to be used in addition.

The mixture to be filtered was introduced into the filter tube by momentarily removing the platinum flask from the oil-bath, after giving it a vigorous shake, and then pouring some of its contents into the tube. By suction on the filter and pressing with a glass rod the solid was obtained as dry as possible; the filter-tube was removed from the hot-water jacket, corked up, and cooled by blowing air on it, and some of the moist solid weighed in a weighing-bottle and then analysed. These operations were in

FIG. 3.



reality not quite as simple as they sound, and introduce several disturbing factors, which probably account for the indications given by the triangular diagram that the nature of the solid phase is not so clearly defined as it might be or as it is with the results for the 25° isothermal. These disturbing factors act in rather different directions according to the concentration of the solution being filtered and the nature of the solid phase. The  $\text{Ca}(\text{OH})_2$  solid phase, owing to its fineness, necessitated the use of an asbestos pad, and the filtration took some time. The weaker solutions in equilibrium with this solid had a considerable vapour pressure, and a certain amount of distillation of water to the cool part of the filter-

tube and loss of moisture during the handling of the moist solid was unavoidable. This we feel sure is the cause of the lines on the triangular diagram for the early portions of the  $\text{Ca}(\text{OH})_2$  curve tending to run too much towards the  $\text{CaO}$  apex of the triangle.

The more concentrated the solutions in equilibrium with calcium hydroxide become, the lower their vapour pressure, and the lines on the triangular diagram then run very closely to the point corresponding with  $\text{Ca}(\text{OH})_2$ . Were there any region of solid solutions, as supposed by Cameron and Robinson, it would be in just about this region that the lines would show the greatest deviation. The  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  solid phase being relatively coarsely crystalline, filtered well, generally only requiring the perforated disk. The lines on the triangular diagram nearly always ran very closely to the correct point for  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ .

In the case of the  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  solid, considerable difficulty was sometimes experienced. This solid tends to be very finely crystalline, and owing to this and the highly concentrated and viscous nature of the equilibrium solution its filtration generally took a considerable time. It tends, moreover, to absorb moisture, and this, no doubt, is the reason for the lines on the triangular diagram tending to run between the points corresponding with  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \text{H}_2\text{O}$ . At first it was thought that the latter hydrate could also exist at  $100^\circ$ ; but all the evidence available is more in favour of the view that the only hydrates at  $100^\circ$  are the dihydrate and  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ . A considerable number of lines on the triangular diagram run to the point corresponding with the latter compound, but hardly any quite to the point for  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \text{H}_2\text{O}$ . No lines have been obtained running between the points for  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  and the anhydrous  $\text{Ca}_2\text{N}_2\text{O}_7$ , so the solid phase can hardly be the latter compound. At the same time it is none too easy to be absolutely sure about half a molecule of water, more or less, in the different circumstances of the experiments.

In the isothermal for  $100^\circ$  given in Fig. 1,  $FG$  is the portion corresponding with  $\text{Ca}(\text{OH})_2$  as solid phase. It will be seen that the maximum amount of free lime in solution is about five times as great as it is at  $25^\circ$ .

The portion  $GHI$  corresponds with the compound  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ . Its point of intersection with the  $\text{Ca}(\text{OH})_2$  curve is at about 1.675 per cent. of free calcium oxide and 57 per cent. of calcium nitrate. At 1.252 per cent. of free calcium oxide and 70.6 per cent. of calcium nitrate it cuts the curve for  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ . The experimental points in the region of the hydrates,  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ , do not fall quite as smoothly on to their respective

curves as could be wished.\* This is partly due to slight uncertainties introduced by the "difference" method of analysis adopted, and also partly owing to the somewhat unfavourable conditions of the titrations of the free lime. Owing to the very high content of the solutions in calcium nitrate, great dilution was necessary in carrying out the titrations in order to eliminate the neutral-salt effect on the indicator as far as possible. This is not favourable to a high degree of accuracy in the titration. It seems quite certain that the hydrate  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , stable at  $25^\circ$ , cannot exist at  $100^\circ$ , for when added to the solutions in the neighbourhood of point *G* it was always transformed completely into the dihydrate.

The trihydrate and the dihydrate cannot unfortunately be distinguished under the microscope, as the crystals have the same general appearance and habit of growth, and evidently only differ very slightly. They form clear, square-ended prisms, often of a fair size, which show straight extinction. Sometimes the ends of the prisms are cut off obliquely.

The compound  $\text{Ca}_2\text{N}_2\text{O}_7 \cdot \frac{1}{3}\text{H}_2\text{O}$  appears entirely different, yielding small prisms which extinguish obliquely, but which are often so modified as to have a general hexagonal outline. They are frequently not very well formed, and somewhat intergrown. In such cases the solid phase has a granular appearance under the microscope. The half hydrate is the stable solid phase along the portion *IK* of the  $100^\circ$  isothermal.

The calcium nitrate is readily distinguished by means of its isotropic crystals belonging to the cubical system. *KL* is the portion of the isothermal corresponding with the anhydrous normal nitrate.

#### Summary.

The nature of the solid phases capable of existing in equilibrium with aqueous solutions of calcium nitrate containing free lime has been studied at  $25^\circ$  and  $100^\circ$ .

Only one well-defined basic nitrate,  $\text{Ca}_2\text{N}_2\text{O}_7$ , has been found, which forms several hydrates.

No series of solid solutions,  $\text{CaO}, x\text{N}_2\text{O}_5, y\text{H}_2\text{O}$ , such as that postulated by Cameron and Robinson (*loc. cit.*), exists either at  $25^\circ$  or  $100^\circ$ .

The work described in the present paper dealing with the  $25^\circ$

\* That this is not due to the small fluctuations of temperature (possibly  $\pm 0.2^\circ$ ) which occurred during the experiments seems to be shown by the fact that in some cases where the temperature was purposely kept half a degree above or below  $100^\circ$  during the whole of the time that the contents of the flask were reaching equilibrium, the experimental points did not fall off the curve to any greater extent than in the other experiments.

isothermal was carried out in the Inorganic Laboratory of the University of Liverpool; that dealing with the 100° isothermal in the Chemical Department of University College, Reading. The platinum flask used for the experiments at 100° was lent by the Chemical Society, being purchased by means of a grant made for the purpose by the Research Fund Committee, to whom the authors express their thanks.

### CLXXXI.—*Ionic Equilibria Across Semi-permeable Membranes.*

By FREDERICK GEORGE DONNAN and ARTHUR JOHN ALLMAND.

IN December, 1910, a note was read by Donnan before the London Physiological Society, in which a preliminary account was given of a simple thermodynamic theory of the equilibria occurring at either side of a membrane separating two solutions of electrolytes, one at least of which contains a salt to which the membrane is impermeable. In a later paper (*Zeitsch. Elektrochem.*, 1911, 17, 572) this theory was developed and applied to various cases, and extended to the potential differences occurring at such a membrane. It was shown, in particular, that if on one side of the membrane there is a salt, CR, which cannot pass through, whilst the salt CA, which can pass through the membrane, is in distribution equilibrium across the membrane, then the relation

$$\frac{[C']_I}{[C']_{II}} = \frac{[A']_{II}}{[A']_I} = \lambda$$

holds good, provided the ions of the salt CA obey the laws of ideal solutions. The net result is that the salt CA becomes unequally distributed on the two sides of the membrane. It was also shown, on similar assumptions, that in such a case the potential difference between the two solutions will be given by the equation

$$\pi_2 - \pi_1 = 0.058 \log \lambda$$

at 18°. In the above formula it has been assumed that the ions C' and A' are univalent.

It was shown that measurements of the osmotic pressures of solutions of substances of the type CR in the presence of dialysable substances like CA would be affected by the unequal distribution of the latter across the semipermeable membrane. This result was confirmed by the experiments of Donnan and Harris (*T.*, 1911, 99, 1554) on mixtures of Congo-red and sodium chloride or sodium

hydroxide. It has also been confirmed by the experimental work of Biltz (*Zeitsch. physikal. Chem.*, 1913, **83**, 625). Donnan also showed that, from the point of view of the membrane-potentials, the membrane behaves like a metallic electrode, reversible with respect to the cation C or the anion A.

Measurements of the potential differences between two aqueous solutions of potassium ferrocyanide separated by a membrane of copper ferrocyanide have been made by Green.\*

The ionic relation given above has been shown to be, at all events, qualitatively true for Congo-red and sodium chloride by B. Novikov (preliminary unpublished experiments) and by Donnan and Harris (*loc. cit.*). As, however, it was deemed advisable to test the relation when using a better defined, non-dialysable anion than that of Congo-red, it was proposed to use potassium ferrocyanide and membranes of copper ferrocyanide, the dialysing salt being potassium chloride. Preliminary experiments (unpublished) carried out by A. Makovetsky showed, again, a qualitative agreement with the theory, the potassium chloride becoming concentrated on the side of the membrane from which ferrocyanide was absent. The present paper consists essentially of an account of more elaborate experiments made in order to test the theory more rigorously, and also of certain closely related potential measurements.

It is desirable here to consider the theory of the distribution equilibrium more fully than was done in the previous papers. When the salt CA is in distribution equilibrium on either side of the membrane, the work required isothermally and reversibly to transfer one gram-molecule from one side to the other must be zero. In expressing this condition mathematically, two cases must be considered, namely, when the (binary) electrolyte is such that its constituents obey the laws of ideal solution, and, secondly, when such is not the case. We shall consider these two cases separately.

Considering, first, the case of a simple binary electrolyte, the constituents of which, namely, cation, anion, and undissociated electrolyte, exhibit "ideal" behaviour, the expression for the work required isothermally and reversibly to transfer one gram-molecule from

solution (1) to solution (2), namely,  $\int_{p_1}^{p_2} v dp$ , where  $p$  = osmotic pressure and  $v$  = volume occupied by one gram-molecule at temperature

$T$ , can be easily shown to be equal to  $RT \log \frac{(c_u)_2}{(c_u)_1}$ , or  $2RT \log \frac{(c)_2}{(c)_1}$ .

\* These experiments, which were begun in October, 1911, were completed in April, 1912, and will shortly be published. Their publication has been unfortunately delayed.

where  $c_u$  = concentration of undissociated electrolyte,  $c_i$  = concentration of cation or anion. If the two solutions are in distribution-equilibrium on either side of a membrane (permeable to the electrolyte considered), the work as calculated above is zero, and therefore

$$\begin{aligned}(c_u)_1 &= (c_u)_2, \\ (c_i)_1 &= (c_i)_2.\end{aligned}$$

Suppose, however, that on one side of the membrane there is present also an electrolyte with a (diffusible) cation common to the foregoing electrolyte, and with a non-diffusible anion. The above relations then become:

$$\begin{aligned}(c_u)_1 &= (c_u)_2 \quad . \quad . \quad . \quad . \quad . \quad (1) \\ (c_k)_1 \cdot (c_a)_1 &= (c_k)_2 \cdot (c_a)_2 \quad . \quad . \quad . \quad . \quad (2)\end{aligned}$$

where  $c_k$  and  $c_a$  denote the concentrations of the cation and anion respectively of the diffusible (permeable) electrolyte, and  $c_u$  the concentration of its undissociated part. In the more general case, where the constituents of the binary electrolyte considered do not obey the laws of ideal solutions, the expression for the work may be written  $RT \log \frac{(a_u)_2}{(a_u)_1}$  or  $RT \log \frac{(a_k)_2 \cdot (a_a)_2}{(a_k)_1 \cdot (a_a)_1}$ , where  $a$  denotes the function termed by G. N. Lewis the "activity."

The conditions for distribution-equilibrium then become:

$$\begin{aligned}(a_u)_1 &= (a_u)_2 \quad . \quad . \quad . \quad . \quad . \quad (3) \\ (a_k)_1 \cdot (a_a)_1 &= (a_k)_2 \cdot (a_a)_2 \quad . \quad . \quad . \quad . \quad (4)\end{aligned}$$

We can experimentally test in any particular case whether the equations (1) and (2) are valid, using the values for the degrees of dissociation calculated from conductivity data.

It is known that in the case of many strong electrolytes the activities of the ions are not proportional to the concentrations (as determined from conductivity data), and that this divergence from proportionality is still greater in the case of the undissociated parts.

There is reason, therefore, to expect that the equations (1) and (2) will yield a qualitative idea of the distribution equilibrium, but may not yield results agreeing quantitatively with the experimental data, the divergence in the case of equation (2) being greater than in that of equation (1).

#### EXPERIMENTAL.

The apparatus employed for determining the distribution ratios was very simple, consisting essentially of osmometer vessels, as used by Donnan and Harris, only without the perforated silver plates and manometer, as no appreciable differences of pressure

were to be withstood or measured. The internal diameter of the cylindrical glass tubes was about 3.5 cm., their length 2.5–3.5 cm., the length of the side-tubes 15 cm., and the volume of the closed apparatus up to the neck about 25–35 c.c. The membranes (of copper ferrocyanide deposited in vegetable parchment) were separated by washers of pure caoutchouc from the edges of the glass cylinders, which had been carefully ground flat, the apparatus being thus rendered tight. The clamping frames used were nickel-plated, and the vessels stood in stout, cylindrical earthenware jars, containing the second solution. This form of apparatus allows of the use of a large active surface of membrane, and reduces to a sufficiently small amount the bulk of the inside liquid which is to come into equilibrium with the outer fluid.

The membranes used were prepared by turning up the edges of a large piece of vegetable parchment, placing it in a large porcelain dish containing a 7 per cent. solution of potassium ferrocyanide crystals, and filling it with a 5 per cent. solution of copper sulphate crystals. After remaining for two days, the solutions were poured out, the membrane washed, and the process repeated, the copper sulphate being this time outside, and the ferrocyanide solution inside, the parchment. After complete formation, the membrane was well washed and kept under water, pieces of suitable size being cut off when required. The time of preparation of membranes made in this way varied from two to seven days. Experience showed that the time of preparation of the membrane had no noticeable effect on the final equilibrium attained in the distribution experiments, and that after four days' treatment with the forming solutions very little further increase in thickness resulted. Two-day membranes, however, whilst impermeable to the passage of ferrocyanide, permitted of an appreciably more rapid attainment of equilibrium.

The procedure adopted at the beginning of the work was to start an experiment by placing a solution containing potassium ferrocyanide only in the outer vessel, and a solution containing potassium chloride only in the membrane vessel, allowing the latter salt gradually to diffuse out, and following the concentration change in the inner vessel by withdrawing 10 c.c. by means of a pipette and titrating with silver nitrate, and replacing subsequently the liquid abstracted by 10 c.c. of a solution of identical concentration. When, finally, the concentration of the inner solution ceased to alter appreciably with time within the limits of experimental error, the experiment was stopped, and the solution in the outer jar analysed. In two or three cases this procedure was checked by starting with pure water in the inner

vessel, and with a mixture of chloride and ferrocyanide in the outer one, the final equilibrium concentration of the potassium chloride concentration in the inner vessel being determined. With vessels of equal volume and with equal total amounts of water, potassium chloride, and potassium ferrocyanide present, the same final equilibrium state should be reached from both sides, and this was found to be the case. In later experiments, when we had already in advance a good idea of the final concentrations which would be reached with given initial conditions, the procedure was shortened by making up the potassium chloride solution in the inner vessel to approximately the final strength expected. In the earlier experiments the membrane vessels were given a vertical up-and-down motion by mechanical means in order to effect stirring, but it was found that the acceleration thus obtained was small, so that in the majority of the experiments the vessels were merely stirred by hand once or twice daily. The time taken by the single experiments varied greatly—between ten and forty days. The following excerpt from the experimental results will be sufficient to show that equilibrium was really obtained. The figures are c.c. of the particular standard silver nitrate solution used.

TABLE I.

Number of experiment.	Days after starting.							
	5	7	8	9	10	12	13	14
11	18.86	19.26	—	19.47	—	19.61	—	19.60
29	—	—	0.96	—	1.14	—	1.34	—
44	5.85	5.94	—	—	5.98	6.00	—	5.99

Number of experiment.	Days after starting.								
	15	17	20	22	24	27	31	34	36
11	—	—	—	—	—	—	—	—	—
29	1.46	1.53	1.62	1.65	1.69	1.70	1.73	1.75	1.76*
44	—	—	—	—	—	—	—	—	—

\* 1.79 when approached from side of more concentrated solution.

Some little time was spent in selecting the most suitable analytical method for determining chloride and ferrocyanide in the same solution. The direct determination of ferrocyanide gave little trouble, results quite accurate enough for our purpose being obtained by titration with potassium permanganate in the presence of sulphuric acid, according to Müller and Diefenthaler's method (*Zeitsch. anal. Chem.*, 1911, 50, 383). The standard permanganate solutions used were approximately equivalent to about 0.1 molar potassium ferrocyanide. According to the amount of ferrocyanide present, 50–100 c.c. of the outer solution were



titrated (always in duplicate), the amount of permanganate required varying between 3.5 and 15 c.c. The presence of chloride did not prevent sharp end-points being obtained, except in the cases of experiments 19 and 20, where the ratio of chloride to ferrocyanide was at its highest and most unfavourable value. In these cases, the odour of chlorine was distinctly apparent before the completion of the titration; otherwise the results can be regarded as trustworthy to within 1 per cent., sufficiently good for our purpose. The degree of accuracy of the method used was checked by the analysis of known mixtures of chloride and ferrocyanide. In order to avoid the errors inherent in an indirect determination of the chloride, attempts were made to determine it directly by distillation with excess of permanganate and sulphuric acid, the evolved chlorine being estimated in the usual way by iodide and thiosulphate. The reaction was found to be very slow, and only partly complete after an hour's boiling, even with magnesite in the flask to sweep out the chlorine. If, however, small quantities of copper, cobalt, or nickel salts were added, the rate of reaction was very much increased. However, when solutions containing ferrocyanide were investigated, the speed of reaction was reduced to a still lower value. In some cases, only 40 per cent. of the chlorine had passed over when the contents of the flask had been distilled down to a paste. In these circumstances, it was decided to titrate chloride and ferrocyanide together with silver nitrate in the presence of potassium chromate, thus arriving at the chloride concentration by difference. This procedure proved rapid and sufficiently accurate, the only case in which we are inclined to suspect any considerable error being in the potassium chloride concentration of experiment 39.

In order to test the effect of small analytical and other experimental errors on the values of the distribution ratios, ten experiments were set up, in which approximately the same initial concentrations of the substances in question were employed, and the equilibrium concentrations determined by the methods described.

TABLE II.

Number of experiment.	$K_1$ FeCy <sub>5</sub> outside.	KCl outside.	KCl inside.	$\frac{[K]}{[K]_{in}}$ out	$\frac{[Cl]}{[Cl]_{out}}$ in
1	0.0192	0.0463	0.0527	1.24	1.14
2	0.0190	0.0457	0.0527	1.23	1.15
3	0.0189	0.0456	0.0521	1.24	1.14
4	0.0189	0.0470	0.0534	1.23	1.14
5	0.0189	0.0449	0.0510	1.25	1.14
6	0.0189	0.0471	0.0522	1.26	1.11
7	0.0192	0.0463	0.0528	1.24	1.14
8	0.0191	0.0468	0.0539	1.22	1.15
9	0.0209	0.0462	0.0538	1.25	1.16
10	0.0189	0.0468	0.0534	1.23	1.14

(The number of c.c. of permanganate used for titration varied between 4.7 and 5.3.) The results are given in table II.

In the above table, [K] and [Cl] indicate concentrations of total potassium and total chlorine respectively.

The above results show that the analytical methods suffice, and that the errors to be expected in the values of the distribution ratios are small. It should be mentioned that, at the conclusion of every experiment, the liquid inside the membrane vessel was tested for ferrocyanide. In the first three series of experiments, the results of which follow, ferrocyanide could not be detected, or else was present in such minute traces that it could not affect the relations which were being investigated. Thus, traces were present in the inside liquids of experiments 4 and 8 of table II, but have obviously had no effect on the distribution ratios. Experiments 41 and 42 of the fourth series, however, were rendered valueless owing to the entrance of ferrocyanide, and the results of another series, in which the concentration of ferrocyanide in the outer liquid was kept higher still (namely, about 0.5 equivalent normal), are all useless on that account, and are therefore not given here. It is possible that a small mechanical leak was the cause of this phenomenon, but we are inclined to think it more likely that a breakdown in the membrane, due to physical or chemical causes, was taking place; or, if one takes the view that the membrane is not in reality perfectly impermeable to the ferrocyanide, the effect of increased ferrocyanide concentration may find its explanation in a very slow diffusion through the membrane.

Another disturbing influence, which made its appearance in the fifth (unquoted) series of measurements, was osmosis of water outwards from the membrane vessel to the strong ferrocyanide solution in the outer vessel. This took place very slowly, if at all, in the series of measurements given in the present paper, and, under such conditions, can be regarded as not appreciably affecting the dual ionic equilibrium.

#### *Results of Distribution Experiments.*

Tables III—VI contain a summary of the experimental results, the concentrations being always given as gram-equivalents per litre. In each table the concentration of the ferrocyanide in the outer vessel is approximately constant throughout, whilst the concentrations of the potassium chloride on both sides of the membrane increase from top to bottom. The last two columns give the relations between the total (not ionic) potassium and chlorine inside and outside, and the ratio  $\frac{[\text{Cl}]_{\text{in}}}{[\text{Cl}]_{\text{out}}}$  gives a measure of the

"expelling" action exerted by the ferrocyanide in the outer vessel. It will be noticed that the effect, which is greater the greater the ratio of ferrocyanide to chloride, can become very large. Thus, in experiment 40, the concentration of chloride on the side of the membrane free from ferrocyanide was three times as great as on the other.

TABLE III.  $[K_4FeCy_6]$  circa 0.01 equivalent normal.]

Experi- ment.	$K_4FeCy_6$ out.	KCl out.	KCl in.	$\frac{[K] \text{ out}}{[K] \text{ in}}$	$\frac{[Cl] \text{ in}}{[Cl] \text{ out}}$
27	0.0086	0.0090	0.0131	1.34	1.45(?)
28	0.0101	0.0098	0.0138	1.44	1.41
26	0.0100	0.0187	0.0225	1.28	1.20
25	0.0093	0.0179	0.0213	1.28	1.19
24	0.0091	0.0449	0.0487	1.11	1.08
23	0.0102	0.0460	0.0497	1.13	1.08
22	0.0106	0.0341	0.0569	1.08	1.03
21	0.0087	0.0539	0.0562	1.07	1.02
19	0.0094	0.2277	0.2278	1.04	1.00
20	0.0097	0.2280	0.2288	1.04	1.00

TABLE IV.  $[K_4FeCy_6]$  circa 0.02 equivalent normal.]

17	0.0189	0.0110	0.0169	1.77	1.54
18	0.0185	0.0112	0.0178	1.67	1.59
13	0.0193	0.0219	0.0283	1.46	1.29
14	0.0188	0.0231	0.0288	1.45	1.25
Mean of 1-10	0.0192	0.0463	0.0528	1.24	1.14
15	0.0197	0.1153	0.1210	1.12	1.05
16	0.0182	0.1186	0.1240	1.10	1.05
11	0.0183	0.2201	0.2234	1.07	1.01
12	0.0185	0.2235	0.2280	1.06	1.02

TABLE V.  $[K_4FeCy_6]$  circa 0.05 equivalent normal.]

29	0.0467	0.0084	0.0201	2.70	2.39
30	0.0496	0.0087	0.0204	2.86	2.34
31	0.0468	0.0161	0.0288	2.18	1.79
32	0.0467	0.0161	0.0287	2.19	1.78
33	0.0488	0.0433	0.0576	1.80	1.33
34	0.0489	0.0465	0.0608	1.87	1.31
35	0.0483	0.0892	0.1026	1.34	1.15
36	0.0181	0.0878	0.1010	0.34	1.15
37	0.0491	0.2211	0.2383	1.15	1.06
38	0.0481	0.2253	0.2380	1.15	1.06

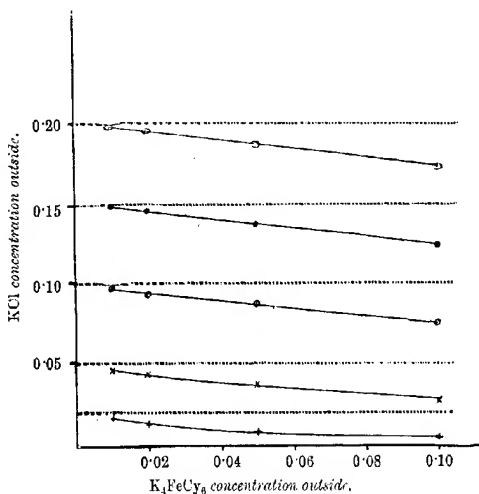
TABLE VI.  $[K_4FeCy_6]$  circa 0.1 equivalent normal.]

39	0.0961	0.0051	0.0252	4.01	4.94(?)
40	0.0946	0.0082	0.0264	3.89	3.22
43	0.0974	0.0437	0.0686	2.06	1.57
44	0.0961	0.0432	0.0684	2.03	1.58
45	0.0983	0.0888	0.1162	1.61	1.31
46	0.1008	0.0921	0.1163	1.66	1.26
47	0.0950	0.2263	0.2538	1.27	1.12
48	0.0973	0.2210	0.2513	1.27	1.14

In almost every case, the ratio in column five exceeds that in column six. In fact, so regular is this behaviour, that we are justified in assuming experimental errors in experiments 27 and 39, where these relations are inverted. Experiment 28 is probably also faulty. It is, of course, just in the experiments at the head of each table, where the chloride concentrations are low, that their determination by difference is likely to lead to multiplication of error.

In order more easily to appreciate the effect of the presence of ferrocyanide on the distribution of the chloride, Figs. 1 and 2 are

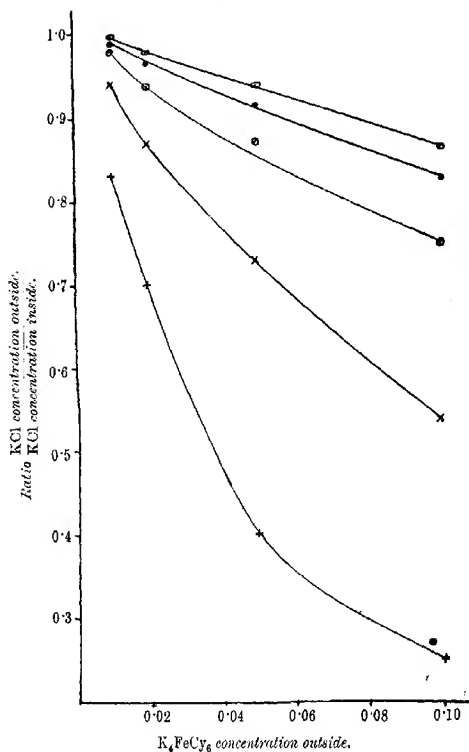
FIG. 1.



given. Fig. 1, which was drawn by graphical interpolation from the results of tables III—VI, gives the relation between the concentrations of ferrocyanide and chloride in the outer vessel for various constant concentrations of chloride in the inner vessel, namely, 0.02, 0.05, 0.10, 0.15, and 0.2 normal. If the ferrocyanide had no effect on the distribution ratio, the concentration of the chloride in the outer vessel for any given concentration of chloride in the inner vessel would naturally be independent of the concentration of the ferrocyanide—remaining, in fact, always equal to the concentration of the chloride in the inner vessel. The increasing divergence from this state of affairs with increasing

concentration of ferrocyanide is clearly shown by the curves given in Fig. 1. Fig. 2 (drawn with the aid of Fig. 1), in which the ratio  $\frac{\text{KCl outside}}{\text{KCl inside}}$  is plotted against concentration of ferrocyanide for a number of constant chloride concentrations in the inside

FIG. 2.



vessel, shows the unequal distribution of the chloride still more clearly, the ordinates deviating more widely from unity the greater the ferrocyanide concentration.

In order to push this effect to extreme limits, a few experiments were carried out, using concentrated ferrocyanide solutions, dis-

turbance due to osmosis being eliminated by adding sucrose to the weaker solution in the inner vessel. The necessary concentrations of sucrose were calculated from the experiments of Tammann, and, so far as the elimination of osmosis was concerned, the results were quite satisfactory. All the potassium chloride was placed in the inner vessels at the start, the jars were stirred at intervals, and the concentration and volume of the inner liquids determined after thirty-two days, it being assumed that equilibrium was then attained. By measuring the volume of the outer liquids, the concentration of the potassium chloride which had diffused out could be calculated, and rough values for the ratio  $\frac{\text{KCl inside}}{\text{KCl outside}}$  obtained.

Unfortunately, in most of these experiments a certain amount of ferrocyanide diffused inwards through the membranes, although the latter were freshly prepared, were very carefully put on, and were as dense as any previously used. Table VII contains the results.

TABLE VII.

$\text{K}_4\text{FeCy}_6$ out.	KCl out.	KCl in.	KCl in KCl out	Remarks.
0.5 <i>n</i> .	0.007 <i>n</i> .	0.0324 <i>n</i> .	4.6	No $\text{K}_4\text{FeCy}_6$ inside.
1.0 <i>n</i> .	0.006	< 0.0433	< 7.2	Small amounts of
1.0 <i>n</i> .	0.0055	< 0.0443	< 8.0	ferrocyanide inside.
2.0 <i>n</i> .	Useless owing to large amounts of ferrocyanide inside.			

#### Discussion of Distribution Equilibria.

From the above experimental data, the ionic ratios with which the theory deals can be calculated. For this purpose, use was made of the following equations (compare Sherrill, *J. Amer. Chem. Soc.*, 1910, **32**, 742):

$$\begin{aligned}
 (a) \quad & \frac{a_1}{1-a_1} = K_1(C_{a_1})^{1-n_1} \\
 (b) \quad & \frac{a_1}{1-a_1} = K_1(C_1a_1 + C_2a_2)^{1-n_1} \\
 (c) \quad & \frac{a_2}{1-a_2} = K_2(C_1a_1 + C_2a_2)^{1-n_2}
 \end{aligned}$$

The suffixes 1 and 2 refer to potassium chloride and potassium ferrocyanide respectively. Equation (a) was used for calculating the degrees of dissociation in the pure potassium chloride solutions, and (b) and (c) for the degrees of dissociation of chloride and ferrocyanide respectively in the mixed solutions:  $a$  represents degree of dissociation,  $C$  equivalent concentration,  $K$  and  $n$  empirical constants, deduced from conductivity measurements, and characteristic of the salts in question. In the present case, the

values of  $K$  and  $n$  taken were as follows (compare Noyes, *J. Amer. Chem. Soc.*, 1908, **30**, 351; Johnston, *loc. cit.*, 1909, **31**, 1010):

$$K_1 = 2.20; n_1 = 1.42.$$

$$K_2 = 0.298; n_2 = 1.45.$$

According to these equations (which can be derived from the isohydric theory of Arrhenius, and have been much used and discussed in recent years by Noyes and his collaborators), in a mixture of two salts with a common ion, each salt has a degree of dissociation equal to that which it has when present alone in a solution the ionic concentration of which is equal to that of the common ion in the mixture. In the present case, the assumption is made that the potassium ferrocyanide ionises directly to  $4K^+$  and  $FeCy_6^{4-}$ , for which assumption, although at first sight unlikely, the results of Johnston afford some support.

It is necessary to solve the above equations by trial and error. The process, although laborious, is straightforward. The results of the calculations are given in tables VIII—XI (corresponding with tables III—VI). The columns contain, reading from left to right, the number of the experiment, the degrees of dissociation of the potassium chloride and potassium ferrocyanide in the mixture, the potassium and chloridion concentrations in the mixture calculated therefrom, the degree of dissociation of the chloride and the potassium and chloridion concentrations in the inner vessel, and, finally, the ionic distribution ratios, which, according to the simple theory, should be identical.

TABLE VIII.

Experi- ment.	Outside.				Inside.			
	$\alpha_1$	$\alpha_2$	$[K^+]$	$[Cl^-]$	$\alpha$	$\frac{[K^+]}{[Cl^-]}$	$\frac{[K^+]_{out}}{[K^+]_{in}}$	$\frac{[Cl^-]_{out}}{[Cl^-]_{in}}$
27	0.925	0.67	0.0141	0.0083	0.935	0.0122	1.15	1.47
28	0.925	0.66	0.0157	0.0091	0.93	0.0128	1.23	1.42
26	0.915	0.625	0.0234	0.0171	0.92	0.0207	1.13	1.21
25	0.915	0.625	0.0222	0.0164	0.92	0.0196	1.13	1.20
24	0.89	0.545	0.0449	0.0400	0.89	0.0433	1.04	1.08
23	0.89	0.545	0.0465	0.0409	0.89	0.0442	1.05	1.08
22	0.86	0.475	0.0860	0.0809	0.86	0.0833	1.03	1.03
21	0.86	0.475	0.0849	0.0807	0.86	0.0827	1.03	1.02
19	0.815	0.39	0.1894	0.1856	0.815	0.1857	1.02	1.00
20	0.815	0.39	0.1896	0.1858	0.815	0.1866	1.02	1.00

TABLE IX.

17	0.92	0.625	0.0219	0.0101	0.925	0.0156	1.40	1.54
18	0.915	0.625	0.0218	0.0102	0.925	0.0165	1.32	1.61
13	0.905	0.59	0.0312	0.0198	0.91	0.0257	1.21	1.30
14	0.905	0.585	0.0319	0.0209	0.91	0.0262	1.22	1.25
1-10	0.885	0.53	0.0511	0.0410	0.89	0.0470	1.09	1.15
15	0.85	0.45	0.1069	0.0980	0.85	0.1028	1.04	1.05
16	0.85	0.45	0.1090	0.1008	0.85	0.1054	1.03	1.05
11	0.815	0.39	0.1869	0.1794	0.82	0.1832	1.02	1.02
12	0.815	0.39	0.1894	0.1822	0.815	0.1858	1.02	1.02

TABLE X.

Experi- ment.	Outside.				Inside.			
	$\alpha_1$	$\alpha_2$	[K].	[Cl].	$\alpha$	[K'] = [Cl']	[K'] <sub>out</sub> , [K'] <sub>in</sub>	[Cl'] <sub>in</sub> , [Cl'] <sub>out</sub>
29	0.90	0.575	0.0344	0.0076	0.92	0.0185	1.86	2.45
30	0.90	0.57	0.0361	0.0078	0.92	0.0188	1.92	2.40
31	0.895	0.56	0.0406	0.0144	0.91	0.0262	1.55	1.82
32	0.895	0.56	0.0405	0.0144	0.91	0.0261	1.55	1.81
33	0.875	0.51	0.0628	0.0379	0.885	0.0510	1.23	1.35
34	0.875	0.505	0.0654	0.0407	0.885	0.0538	1.22	1.32
35	0.855	0.46	0.0985	0.0763	0.86	0.0882	1.12	1.16
36	0.855	0.46	0.0972	0.0751	0.86	0.0869	1.12	1.16
37	0.81	0.38	0.2019	0.1833	0.815	0.1946	1.04	1.06
38	0.81	0.38	0.2008	0.1825	0.815	0.1940	1.04	1.06

TABLE XI.

39	0.88	0.525	0.0549	0.0045	0.915	0.0231	2.38	5.14
40	0.88	0.52	0.0564	0.0072	0.915	0.0242	2.33	3.33
43	0.86	0.475	0.0838	0.0376	0.88	0.0604	1.39	1.61
44	0.865	0.475	0.0830	0.0374	0.88	0.0602	1.38	1.61
45	0.845	0.44	0.1183	0.0750	0.855	0.0993	1.19	1.32
46	0.84	0.44	0.1217	0.0774	0.855	0.0994	1.21	1.28
47	0.805	0.37	0.2163	0.1812	0.81	0.2056	1.05	1.13
48	0.81	0.37	0.2150	0.1790	0.81	0.2035	1.06	1.14

It is clear, however, from the above tables that the ionic ratios are not equal. In tables III—VI the "total potassium" ratio exceeded the "total chlorine" ratio; here, however, the "ionic potassium" ratio is less than the "ionic chlorine" ratio, except in a few experiments at the bottom of tables VIII and IX. If we assume that the ions obey the laws of ideal solutions, two causes for this discrepancy might be possible. In the first place, the ionic concentrations deduced from conductivity data may be seriously incorrect, owing to the need of a correction for viscosity (Washburn, *J. Amer. Chem. Soc.*, 1911, **33**, 1462). In the present case this seems unlikely, since the viscosities of solutions of potassium chloride and potassium ferrocyanide of the concentrations used in the present investigation differ very slightly from the viscosity of water (Reyher, *Zeitsch. physikal. Chem.*, 1888, **2**, 744; Wagner, *ibid.*, 1890, **5**, 37), whereas the discrepancies to be accounted for are considerable. Moreover, a few experiments made with pure water, with a potassium chloride solution and with a mixed solution of chloride and ferrocyanide (both solutions of the same composition as the final equilibrium solutions of experiments 1—10), showed that there was nothing abnormal in the viscosity of mixtures of chloride and ferrocyanide. The extreme differences in the values observed (the experiments were carried out with a Scarpa viscometer [*Gazzetta*, 1910, **40**, ii, 271] similar to the one used by F. D. Farrow [*T.*, 1912, **101**, 347]) did not exceed 0.5 per cent., and therefore it did not appear likely that viscosity correc-



tions applied to the conductivity data would lead to ionisation values seriously differing from those used in the present paper.

In the second place, it is possible that an appreciable part of the conductivity of potassium ferrocyanide solutions is due to intermediate ions; that is to say, the salt does not ionise directly to  $4K^+$  and  $FeCy_6^{4-}$ , but that appreciable amounts of such ions as  $K_3FeCy_6$ ,  $K_2FeCy_6$ , etc., are present. As this, however, would make the discrepancy between the ratios greater, and not less, such a supposition cannot explain the divergence in question.

The most probable explanation appears to be that the constituents of the salts do not obey the laws of ideal solutions, and that therefore the ionic ratios are not proportional to the activity ratios, which latter appear in the correct equations (see introduction). It has been shown by A. A. Noyes, G. N. Lewis, and their collaborators that the undissociated part of a strong electrolyte deviates more from the laws of ideal solutions than the ionised part. Now, as was pointed out in the introduction, if there exists distribution equilibrium, then

$$\begin{aligned} (a_u)_1 &= (a_u)_2 \\ (a_K)_1 \cdot (a_{Cr})_1 &= (a_K)_2 \cdot (a_{Cr})_2 \end{aligned}$$

We should therefore expect in the present case that the equation

$$[\text{undissociated KCl}]_1 = [\text{undissociated KCl}]_2$$

would hold less strictly than the equation

$$[K^+]_1 \cdot [Cl^-]_1 = [K^+]_2 \cdot [Cl^-]_2$$

The following tables, calculated from the data of tables VIII—XI, show that this is indeed the case. Column four gives the ratio of the concentrations of the undissociated parts, and column five the ratio of the ionic products, as calculated from conductivity data.

TABLE XII.

Experiment.	Undissociated KCl inside.	Undissociated KCl outside.	Ratio of undissociated parts.	Ionic product ratio.
27	0.00085	0.00068	1.25	1.28 (?)
28	0.00097	0.00074	1.31	1.16
26	0.00180	0.00159	1.13	1.07
25	0.00170	0.00149	1.14	1.06
24	0.00536	0.00494	1.08	1.04
23	0.00547	0.00506	1.08	1.03
22	0.0136	0.0132	1.03	1.00
21	0.0135	0.0131	1.02	0.99
19	0.0421	0.0421	1.00	0.98
20	0.0423	0.0422	1.00	0.98

TABLE XIII.

Experiment.	Undissociated KCl inside.	Undissociated KCl outside.	Ratio of undis- sociated parts.	Ionic pro- duct ratio.
17	0.00127	0.00088	1.44	1.10
18	0.00134	0.00095	1.41	1.22
13	0.00255	0.00208	1.22	1.07
14	0.00259	0.00219	1.18	1.02
1—10	0.00581	0.00532	1.09	1.06
15	0.0181	0.0173	1.05	1.01
16	0.0186	0.0178	1.04	1.02
11	0.0402	0.0407	1.01	1.00
12	0.0422	0.0413	1.02	1.00

TABLE XIV.

29	0.00161	0.00084	1.92	1.32
30	0.00163	0.00087	1.87	1.25
31	0.00259	0.00169	1.53	1.17
32	0.00258	0.00169	1.53	1.17
33	0.00662	0.00341	1.22	1.10
34	0.00699	0.00581	1.20	1.08
35	0.0144	0.0129	1.11	1.04
36	0.0141	0.0127	1.11	1.04
37	0.0442	0.0430	1.03	1.02
38	0.0440	0.0428	1.03	1.02

TABLE XV.

39	0.00214	0.00061	3.51	2.16
40	0.00224	0.00098	2.29	1.43
43	0.00823	0.00612	1.34	1.16
44	0.00821	0.00583	1.41	1.17
45	0.0168	0.0138	1.22	1.11
46	0.0169	0.0147	1.14	1.06
47	0.0482	0.0451	1.07	1.08
48	0.0478	0.0420	1.14	1.08

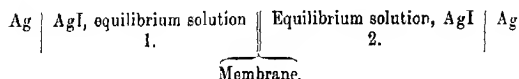
The divergence from unity in column four is, in general, greater than that in column five.

#### *Electromotive Force Measurements.*

The first series of measurements was made with the object of testing the theory referred to previously (*Zeitsch. Elektrochem.*, 1911, 17, 572). According to this theory, if there exists distribution-equilibrium in a case where the concentrations of the diffusible ions are unequal on either side of the membrane, then there must exist a potential difference between these solutions.

If the ions obey the laws of ideal solutions, this potential difference will be proportional to the logarithm of the ratio of the concentrations of the diffusible ions. If, on the other hand, the ions do not obey the laws of ideal solution, the potential difference will be proportional to the logarithm of the ratio of the activities.

The first measurements were made with electrodes reversible with respect to the anion. It was intended, first, to use mercury electrodes with calomel as depolariser, as in the ordinary calomel electrode, but it was found that the mercurous chloride reacted with the ferrocyanide, and caused disturbances. Silver electrodes with silver chloride as depolariser could also not be used, as, owing to the greater insolubility of silver ferrocyanide, the silver chloride was converted into the latter salt by the potassium ferrocyanide. As might be expected from the greater insolubility of silver iodide, it was found that the latter was not affected by solutions of potassium ferrocyanide and potassium iodide, in which the potassium iodide was present in amounts equivalent to the potassium chloride in the equilibrium solutions. This held, at all events, for the majority of such solutions in which the ratio of ferrocyanide to iodide was not too high. It occurred to us, therefore, that potassium iodide in equivalent amount might be substituted in the equilibrium mixtures for the chloride actually employed in the equilibrium experiments, since the ionisation-coefficients of these two salts are probably very similar. Accordingly, the following combination was measured:



In the above combination, the *E.M.F.* at 18° due to the end electrodes is given by the expression  $0.058 \log \frac{(a_{I^-})_1}{(a_{I^-})_2}$ , and the corresponding *E.M.F.* due to the membrane by the expression  $0.058 \log \frac{(a_{I^-})_2}{(a_{I^-})_1}$ . It is clear, therefore, that if the solutions, and therefore the *I*<sup>-</sup> ions, are in equilibrium across the membrane, the total *E.M.F.* will be zero. The different combinations were measured in series with a standard cell. The results are contained in table XVI.

TABLE XVI.

Number of experiment in tables III—VI.	<i>E.M.F.</i> (positive current from solution free from ferrocyanide to mixed solution outside cell)
19 and 20	Very small
37 " 38	Very small
1 " 10	—1.5 millivolt
13 " 14	—1.5 "
17 " 18	—4.5 "
31 " 32	—4.5 "
29 " 30	—9.5 "
40	Indefinite

It will be evident from these figures that the *E.M.F.*'s of these combinations are not zero, as would follow from the theory outlined above, if the solutions were in distribution equilibrium. The discrepancies are greater the greater the ratio of ferrocyanide to iodide.

In order to test this point further, experiments were made with electrodes reversible with respect to the cation, namely, potassium. For this purpose, the potassium amalgam electrodes employed by Lewis and Keyes (*J. Amer. Chem. Soc.*, 1912, **34**, 119) were used, the electrolytes being the same as in table XVI. The amalgam employed contained about 0.2 per cent. of potassium. It was prepared and manipulated as described by Lewis and Kraus (*J. Amer. Chem. Soc.*, 1910, **32**, 1459). In some cases a certain amount of disturbance was caused by chemical action of the electrolyte on the amalgam. This was generally the more marked the weaker the solutions in question, and was invariably greater in the solutions containing ferrocyanide. The freer, however, the surface of the amalgam was from gas bubbles, the more closely did the *E.M.F.*'s of the systems measured approach the value zero. In the last two experiments, where the evolution of gas tended to be strong, we allowed the amalgam to flow out slowly and continuously, and in this way, as will be seen, were able to reduce the *E.M.F.* of the system to zero. The results of our measurements are collected in table XVII. It may be concluded that, in the absence of all gas evolution, the *E.M.F.*'s would be, in every case, zero.

TABLE XVII.

Number of experiment in tables III.—VI.	<i>E.M.F.</i> (current from ferrocyanide-free solution to mixed solution outside cell).	Remarks.
19—20	—0.5 millivolt	Slight gas evolution in mixed solution.
27—38	0.0	No gas bubbles.
1—10	—1.0	Very slight gas evolution.
13—14	—0.5 to zero	Very slight gas evolution.
17—18	—1.5	Much gas evolution.
31—32	—1.0	Very variable. Gas evolution.
29—30	Zero	Continuous flow. Negative values of several millivolts when gas evolved.
40	Zero	

These measurements show that, under these conditions, the membrane acts as a reversible electrode with regard to potassium, and that therefore the potential existing at it is proportional to the

logarithm of the ratio of activities of the potassium in the two solutions. If, however, the solutions measured were really in distribution equilibrium, in which case the relation

$$[a_K] \cdot [a_V]_I = [a_K]_{II} \cdot [a_V]_{II}$$

would hold, then the *E.M.F.*'s of the combinations in table XVI would also be zero, which is not the case. We are driven, therefore, to the conclusion that the substitution of potassium iodide for potassium chloride in equivalent concentration results in solutions which, although ionically equivalent, are not in distribution equilibrium.

In order to settle this matter, cells of the following type were set up and measured:

Potassium amalgam | Solution I, silver iodide | Silver

Potassium amalgam | Solution II, silver iodide | Silver

where solutions I and II represent a pair of those solutions, one containing potassium iodide alone and the other a mixture of potassium ferrocyanide and iodide, which we have supposed to be in equilibrium. The value  $e_I - e_{II}$ , where  $e_I$  and  $e_{II}$  are the electromotive forces of the two cells in question, is proportional to the work required isothermally and reversibly to transfer one gram-molecule of potassium iodide from one solution to the other. If the solutions are really in distribution equilibrium, this work will be zero, and therefore the *E.M.F.*'s will be equal. The results are contained in the following table.

TABLE XVIII.

Corresponding experiment of tables III—VI.	Mixed solution, <i>E.M.F.</i> (in volts).	Iodide solution, <i>E.M.F.</i> (in volts).
1—10	1.888	1.885—1.886
17—18	1.943—1.944	1.938—1.939
29—30	1.935	1.927

The inequality of the *E.M.F.*'s of the pairs of cells given in the above table, columns two and three, appears to show that the pairs of solutions concerned are not in equilibrium. A possible explanation of this is that the functional relationship between activity and concentration for iodidions and undissociated potassium iodide is not the same as for chloridions and undissociated potassium chloride. The pairs of solutions containing potassium iodide which we have employed in these *E.M.F.* measurements will not, therefore, be in distribution equilibrium with regard to either potassiums or iodidions. According to the theory given previously, the potential difference across the membrane would therefore not be expected to be proportional to the logarithm of the ratio of the activities of either the potassiums or

the iodidions. Consequently, the *E.M.F.*'s of the cells containing the copper ferrocyanide membrane and either a pair of potassium or a pair of silver-silver iodide electrodes (see tables XVII and XVI respectively) should not be zero. It is therefore singular that the *E.M.F.*'s of the former cells are, as the experiments show, in reality zero, or very nearly so. A possible explanation of this result is that the copper ferrocyanide membrane, owing to its containing, dissolved or adsorbed, a certain quantity of potassium ferrocyanide, acts as a reversible electrode with respect to potassions, irrespective of whether the solutions are in equilibrium or not.\* If we accept this explanation, it follows at once that, in the present case, the membrane cells containing the pair of silver-silver iodide electrodes cannot show a zero *E.M.F.*, for since

$$\frac{[a_{K^+}]_1}{[a_{K^+}]_2} \neq \frac{[a_{I^-}]_2}{[a_{I^-}]_1},$$

it follows that the potential difference across the membrane cannot be proportional to the logarithm of the ratios of the activities of the iodidions, and therefore this potential difference cannot equilibrate that due to the potential difference of the pair of silver-silver iodide electrodes.

A rough calculation of the total *E.M.F.*'s of the membrane cells with silver-silver iodide electrodes can be made in the following manner.

We can write, in general,

$$\begin{aligned} \frac{(a_{K^+})_1}{(a_{K^+})_2} &= l \frac{[K^+]_1}{[K^+]_2} \\ \frac{(a_{I^-})_1}{(a_{I^-})_2} &= m \frac{[I^-]_1}{[I^-]_2}, \end{aligned}$$

where the *a*'s denote activities and the square brackets ionic concentrations, and where *l* and *m* are two unknown factors which are, in general, different from each other and from unity (and may vary with concentration). If, however, we write approximately *l*=*m*=1, then we can at once calculate the potential-difference due to the pair of silver-silver iodide electrodes from the ordinary simple theory, since we know the concentrations of the iodidions in the two solutions (assuming these to be equal to the concentrations of the chloridions in the equivalent equilibrium solutions). We can also calculate in a similar manner the potential-difference at the membrane, since we know from our experimental results that this membrane acts as a reversible

\* Some support is lent to this explanation by certain rather rough measurements published by Bentner (*J. physical Chem.*, 1918, 17, 344) since this work was undertaken.

potassium electrode. The algebraic sum of these two potential differences will give the calculated (approximate) value of the total *E.M.F.* of the membrane cell in question.

The following table (XIX) contains the calculated and experimentally observed *E.M.F.*'s.

TABLE XIX.

*E.M.F.'s of Membrane Cells with Ag—AgI Electrodes.*

Experiment.	Observed <i>E.M.F.</i> (millivolts).	Calculated <i>E.M.F.</i> (millivolts).
Nos. 19—20	<1.0	—0.5
„ 37—38	<1.0	+0.5
„ 1—10	+1.5	+1.3
„ 13—14	+1.5	+1.2
„ 17—18	+4.5	+3.6
„ 31—32	+4.5	+4.0
„ 29—30	+9.5	+6.3

The results are not quite regular, but it will be seen that there is a rough agreement between the two sets of values.

The experimental results contained in tables XVI and XVIII have been tentatively explained on the assumption that the substitution of potassium iodide in equivalent concentration for the potassium chloride of the solutions shown to be in distribution equilibrium produces solutions which are not in distribution equilibrium, because

$$\frac{(a_{\text{I}})_1}{(a_{\text{I}})_2} \text{ is not equal to } \frac{(a_{\text{Cl}})_1}{(a_{\text{Cl}})_2} \text{ when } \frac{[\text{I}^-]_1}{[\text{I}^-]_2} = \frac{[\text{Cl}^-]_1}{[\text{Cl}^-]_2}$$

This assumption admits of a further test in the following way. The *E.M.F.*'s at 18° of the cells with pairs of silver-silver iodide electrodes (table XVI) are given by the general formula

$$E = 0.058 \log \frac{(a_{\text{K}})_1 \cdot (a_{\text{I}})_1}{(a_{\text{K}})_2 \cdot (a_{\text{I}})_2}$$

Taking the *E.M.F.*'s of the cells with potassium amalgam and silver-silver iodide electrodes in pairs (columns two and three of table XVIII), we must also have

$$e_1 - e_2 = 0.058 \log \frac{(a_{\text{K}})_1 \cdot (a_{\text{I}})_1}{(a_{\text{K}})_2 \cdot (a_{\text{I}})_2}$$

and therefore  $E = e_1 - e_2$  in each case.

The results of this comparison are shown in the following table.

TABLE XX.

Experiment.	<i>E</i> (from table XVI) millivolts.	$e_1 - e_2$ (from table XVIII), millivolts.
Nos. 1—10	1.5	2.5
„ 17—18	4.5	5.0
„ 29—30	9.5	8.0

The concordance of columns two and three of this table, although perhaps not as good as might have been expected, is sufficient to render our explanation of the results given in tables XVI and XVIII a possible one.

Writing

$$\frac{(a_i)_1}{(a_i)_2} = m \frac{[I']_1}{[I']_2}$$

and

$$\frac{(a_{cv})_1}{(a_{cv})_2} = n \frac{[Cl']_1}{[Cl']_2}$$

the experimental results given in this paper enable the values of the ratio  $m/n$  to be calculated in a few cases. For, comparing a pair of iodide-(iodide+ferrocyanide) solutions with the corresponding equivalent pair of chloride-(chloride+ferrocyanide) equilibrium solutions (in which the chloridion-concentrations may be supposed to be very approximately equal to the iodidion-concentrations of the corresponding iodide solutions), we have

$$\frac{(a_K)_1 \cdot (a_I)_1}{(a_K)_2 \cdot (a_I)_2} = \frac{m}{n} \frac{(a_K)_1 \cdot (a_{cv})_1}{(a_K)_2 \cdot (a_{cv})_2} = \frac{m}{n}.$$

Hence,  $E = e_1 - e_2 = 0.058 \log m/n$ .

Taking the means of the values of  $E$  and  $e_1 - e_2$ , given in table XX, we arrive at the following results.

TABLE XXI.

Experiment.	Log $m/n$ .	$m/n$ .
Nos. 1—10	0.047	1.114
„ 17—18	0.082	1.208
„ 29—30	0.150	1.413

As regards the accuracy of these values of  $m/n$ , the value 1.4 obtained from experiments 29—30 cannot be in error by more than 5 per cent. Larger errors may, however, occur in the other values, where the measured  $E.M.F.$ 's were smaller. It is fairly certain, therefore, that the value of  $m/n$  calculated in this way diverges largely from unity. It may be observed, also, that these divergences all occur in solutions of chloride and iodide which are dilute with respect to both ferrocyanide and haloid, and increase with the concentration of ferrocyanide. Values of  $m/n$  so divergent from unity appear rather improbable, so that the view expressed above, namely, that the iodide-(iodide+ferrocyanide) systems are not in distribution equilibrium, whilst the equivalent chloride-chloride+ferrocyanide systems are (for the reasons that the chloridions and iodidions deviate differently from the laws of ideal solutions), leads to a position which appears untenable if our experimental results are correct and correctly interpreted.



There would seem to be five possible solutions of this difficulty, namely, the assumption that: (1) the equivalent chloride and iodide solutions differ markedly in degrees of ionisation; (2) the chloride-chloride + ferrocyanide systems are not in distribution equilibrium; (3) the silver-silver iodide electrodes have given erroneous results; (4) the analytical data of the distribution experiments are seriously in error; (5) the phenomena occurring at the semipermeable membrane are not as simple as supposed.

We may exclude (1) as very unlikely, since, although the equivalent chloride and iodide solutions may differ to some extent in degree of ionisation, the differences would be too small to account for the observed results. We may also exclude (4), as the errors inherent in the analytical methods were very carefully examined. With regard to (3), although the silver-silver iodide electrodes did not give quite constant results, yet the measured *E.M.F.*'s could not possibly be erroneous to the extent required. It is very probable that the distribution results correctly represent the phenomena as occurring under the experimental conditions chosen, and therefore in this sense we may exclude (2). The observed deviations from the simple theory of the membrane action, both in the case of the distribution and the *E.M.F.* measurements, increase with the concentration of the ferrocyanide, so that assumption (5), which in a certain sense also includes (2), may be the correct explanation. We are, in fact, as a result of the present work, inclined to take this view, but further experiments with simpler systems will be necessary to establish it. Such experiments are now in progress. For example, we have some evidence, particularly in the case of the more concentrated ferrocyanide solutions, that the latter salt may in reality be slowly diffusing through, so that the conditions in the membrane itself may be variable and relatively complex, instead of constant and simple, as is supposed in the theory given in the early part of this paper.<sup>8</sup>

Apart, however, from all these quantitative considerations, the definite reality of the phenomenon of unequal distribution has been established beyond question by the experiments which we have made. It is highly probable, therefore, that phenomena of this class must play an important part in many physiological processes, and the data given in this paper suffice to exhibit the nature and extent of these phenomena.

<sup>8</sup> Possibly adsorption of salts by the colloidal ferrocyanide may also be a disturbing factor.

*Summary.*

(1) Experiments have been made on the distribution of potassium chloride between two compartments separated by a copper ferrocyanide diaphragm, one compartment of which contained potassium ferrocyanide.

(2) The higher concentration of potassium chloride on the side free from potassium ferrocyanide, and the relation of this unequal distribution to the concentration of the chloride and ferrocyanide, have been experimentally established.

(3) The results obtained agree, in general, with the view of membrane equilibria proposed by Donnan, but a discussion of the distribution data combined with electromotive-force measurements appears to show that, at all events in the case of a copper ferrocyanide membrane and potassium ferrocyanide solutions, the phenomena are not so simple as supposed in the theory mentioned.

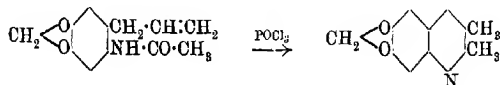
UNIVERSITY OF LIVERPOOL,  
AND UNIVERSITY COLLEGE, LONDON.

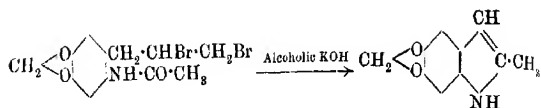
CLXXXII.—*Some Derivatives of Safrole.*

By ROBINSON PERCY FOULDS and ROBERT ROBINSON.

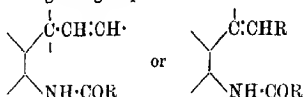
THIS investigation arose from a desire to utilise for synthetical purposes those readily accessible aromatic substances, which, like safrole, eugenol, and apiole, are phenol ethers containing an allyl, propenyl, or, in some cases, a butenyl side-chain. The first case taken was that of safrole, and the present account is of the product of nitration of this substance and of certain compounds which are readily obtained by subsequent simple processes.

6-Nitrosafrole (see p. 1965 for the proof of constitution) is readily reduced in the usual manner, yielding 6-aminosafrole, the acetyl derivative of which is converted by bromine into a normal dibromide. Acetylaminosafrole and acetylaminosafrole dibromide, when treated with phosphoryl chloride and alcoholic potassium hydroxide respectively, undergo transformations of the type for which a search was being made. The nature of these reactions is illustrated in the schemes which follow:

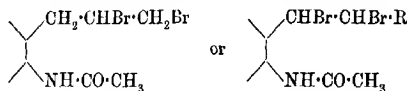




In the case of the production of the indole derivative, as also in that of methylenedioxydimethylquinoline, there is obviously a movement of an ethylene linking from a side-chain to the ring. The yields obtained in these processes are satisfactory, and the reactions are probably capable of general application, and any compound containing the group

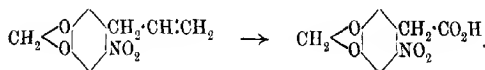


may yield a quinoline derivative on treatment with phosphoryl chloride, or any substance containing the group

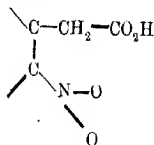


an indole on treatment with alcoholic potassium hydroxide.

Although safrole and eugenyl methyl ether give very poor yields of the corresponding phenylacetic acids on oxidation with potassium permanganate, yet nitrosafrole was converted by this agent in acetone solution into 6-nitropiperonylacetic acid as the sole product:

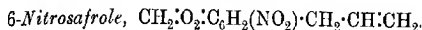


The result may perhaps be explained by a consideration of the distribution of affinity in the molecule of the latter substance, in accordance with the views of Werner. In the following skeleton formula the thickened lines represent affinities strengthened by the nitro-group, and it will be seen that the point of attack for further oxidation would most probably be between the aromatic nucleus and the methylene group, and, as a consequence, the molecule would suffer profound decomposition:



An account is also included of the preparation of *piperonyl-acetylene*. It is a solid melting at 42–43°, and is obtained by the action of alcoholic potassium hydroxide at 125° on bromoisosafrole, produced by the distillation of *isosafrole* dibromide.

## EXPERIMENTAL.



The reaction between safrole and nitric acid is very vigorous, and many unsuccessful trials were made before the following nitration process was adopted.

Safrole (40 grams) dissolved in glacial acetic acid (160 c.c.) was cooled in a mixture of ice and salt, and nitric acid (D 1.42; 32 grams) gradually added with constant shaking. After allowing to remain for two hours, water and ether were added, and the ethereal solution was washed with sodium carbonate, dried, and evaporated. On cooling in the ice-chest the brownish-red, oily residue gradually crystallised. Liquid impurities were removed from the product by contact with porous porcelain, and the nitrosafrole was recrystallised by adding light petroleum to its concentrated ethereal solution. The yield was 60 per cent. of the theoretical. 6-Nitrosafrole crystallises in pale yellow needles, which melt at 25°:

0.1718 gave 0.3665  $\text{CO}_2$  and 0.0706  $\text{H}_2\text{O}$ .  $\text{C}=58.1$ ;  $\text{H}=4.5$ .

0.1440 „ 8.4 c.c.  $\text{N}_2$  at 13° and 761 mm.  $\text{N}=6.9$ .

$\text{C}_{10}\text{H}_8\text{O}_4\text{N}$  requires  $\text{C}=58.0$ ;  $\text{H}=4.3$ ;  $\text{N}=6.8$  per cent.

The substance is readily soluble in all organic solvents with the exception of light petroleum. It dissolves in concentrated sulphuric acid to a bright red solution.

*Oxidation of Nitrosafrole. Production of 6-Nitropiperonyl-acetic Acid.*

Nitrosafrole (9 grams) was dissolved in acetone (60 c.c.) and oxidised by the gradual addition of a solution of potassium permanganate (30 grams in 600 c.c. of water). The acetone was removed by evaporation, and the liquid filtered and acidified with hydrochloric acid. The cooled solution deposited yellow crystals, together with a small amount of tarry material. After several crystallisations from water with the aid of animal charcoal the acid was obtained in pale yellow leaflets (flat needles), rather sparingly soluble, even in hot water, and melting at 183°. The yield of the acid was very satisfactory for an oxidation process:

0.1701 gave 0.3004  $\text{CO}_2$  and 0.0509  $\text{H}_2\text{O}$ .  $\text{C}=48.0$ ;  $\text{H}=3.3$ .

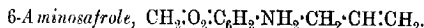
$\text{C}_9\text{H}_7\text{O}_6\text{N}$  requires  $\text{C}=48.0$ ;  $\text{H}=3.1$  per cent.

0.1237 required for neutralisation 0.00462 NaOH, whereas this amount of a monobasic acid,  $C_9H_7O_6N$ , requires 0.00468 NaOH.

It was found impossible further to oxidise this acid to a nitropiperonylic acid, since under a variety of conditions the substance was either recovered unchanged or converted into substances of very much simpler composition. The position of the nitro-group was, however, established by the following observations:

On heating strongly with glycerol, a small amount of a neutral substance, melting after crystallisation from methyl alcohol at  $82^\circ$ , was obtained. This was evidently identical with the 6-nitropiperonylmethane obtained by Angeli and Rimini (*Gazzetta*, 1896, 25, ii, 209), m. p.  $83^\circ$ .

But even so, the position of the nitro-group was not proved in the latter substance. Nitropiperonal condenses with hippuric acid in the normal manner in the presence of sodium acetate and acetic anhydride, and the condensation product on boiling with aqueous sodium hydroxide yields as one of the products of the decomposition the substance melting at  $82^\circ$ . The melting point of a mixture made from the specimens derived from nitrosafrole and from nitropiperonal was  $82^\circ$ . Nitropiperonal yields 6-nitropiperonylic acid on oxidation, and this acid has been converted into hydrastic acid, the constitution of which has been proved.



In preparing aminosafrole it is essential to employ not much more than the stated quantities in any one operation. Nitrosafrole (5 grams), together with concentrated hydrochloric acid (20 c.c.) and granulated tin (12 grams), was heated on a boiling-water bath, and the reaction not checked in any way. When the reduction was finished (several such experiments were combined) the solution was diluted with water, and rendered strongly alkaline by means of sodium hydroxide. The amine was extracted with ether, the dried ethereal solution evaporated, and the residue distilled under diminished pressure. In this first distillation frothing was troublesome, and everything which passed over above  $120^\circ/15$  mm. was collected. The substance was again distilled under the same pressure, and the fraction  $160\text{--}170^\circ$  collected. This was diluted with dry ether, and the solution allowed to remain some hours in the ice-chest, when a colourless, crystalline compound separated, and was removed by filtration. The ethereal solution was again distilled, and the pure amine obtained as a colourless oil boiling at  $168^\circ/15$  mm.:

0.1280 gave 0.3174  $CO_2$  and 0.0735  $H_2O$ .  $C = 67.6$ ;  $H = 6.4$ .

$C_{10}H_{11}O_2N$  requires  $C = 67.8$ ;  $H = 6.2$  per cent.

6-Aminosafrrole crystallises when cooled in a freezing mixture, but melts again on approaching the ordinary temperature. On exposure to air the colourless oil gradually becomes converted into a black, tarry mass. The base is readily soluble in organic solvents, and to some extent in water, but is only to a small extent volatile in steam. Its salts are sparingly soluble; the *hydrochloride* crystallises from water in colourless needles, and the *sulphate* is sparingly soluble in alcohol and may be used for the purification of the amine. 6-Aminosafrrole in aqueous suspension gives an intense violet coloration and precipitates with ferric chloride in the cold, while on boiling the precipitate turns brown, and the steam contains a substance with an odour of *p*-benzoquinone.

*Safroleazo-β-naphthol*.—The base may be quantitatively diazotised, and the diazonium chloride is rather stable, and not quickly decomposed on boiling the solution. With *β*-naphthol and sodium acetate an azo-dye is produced, and separates from acetic acid in deep crimson, flat needles, with green metallic reflex, melting at 166–167°. This colouring matter dissolves in sulphuric acid to an intense blue solution. When a solution of safolediazonium chloride was warmed with alkaline stannous chloride the odour of safrrole became apparent.

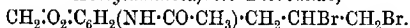
6-Acetylaminosafrrole,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NH}\cdot\text{CO}\cdot\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ .—This derivative is readily obtained by mixing equal volumes of the base and acetic anhydride, when heat is developed and the mass becomes solid. After decomposing the excess of acetic anhydride by water, the substance was collected, and crystallised from methyl alcohol, being so obtained in slender, colourless needles melting at 163°:

0.1778 gave 0.4278  $\text{CO}_2$  and 0.1018  $\text{H}_2\text{O}$ . C=65.6; H=6.3.

$\text{C}_{12}\text{H}_{18}\text{O}_3\text{N}$  requires C=65.75; H=5.9 per cent.

The substance is sparingly soluble in alcohol, and crystallises with readiness, so that in its preparation it is unnecessary to purify the amine as described above, the crude oil being simply mixed with acetic anhydride.

*Acetylaminosafrrole Dibromide,*



This compound is conveniently obtained under the following conditions: Acetylaminosafrrole (5 grams) was dissolved in hot chloroform (30 c.c.), and the solution cooled with stirring so as to obtain the crystals, which separate in a fine state of division. A solution of bromine (3.7 grams) in chloroform (2.5 c.c.) was then gradually added. The acetylmino-compound dissolved, and the dibromide crystallised out, and, when the reaction appeared to be complete,

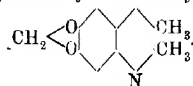
was collected. A further quantity was obtained by evaporation of the solvent and treatment of the residue with methyl alcohol. It was found that even when an excess of the solution of bromine in chloroform was employed no compound other than the dibromide was obtained. The derivative was crystallised from ethyl alcohol, and obtained in characteristically slender needles, quite colourless, and melting at  $191^{\circ}$ . It is sparingly soluble in alcohol, ether, or chloroform:

0.1239 gave 0.1254 AgBr. Br=42.2.

$C_{12}H_{13}O_3NBr_2$  requires Br=42.9 per cent.

*By-product obtained in the Reduction of 6-Nitrosafrole.*—This substance, as already mentioned above, was separated from the twice-distilled 6-aminosafrole by taking advantage of its sparing solubility in ether. It was crystallised by solution in methyl alcohol, in which it is readily soluble in the cold, and precipitation with ether. The colourless needles melted and decomposed at  $215^{\circ}$ . Unfortunately, the quantity obtained was too small to enable us to make a satisfactory examination of the composition of the substance, but it is neutral, and imparts an orange colour to a pine-shaving moistened with hydrochloric acid. This would seem to involve the occurrence of an indole nucleus in its molecule, although, on the other hand, the compound yielded no coloration with *p*-dimethylaminobenzaldehyde.

6:7-Methylenedioxy-2:3-dimethylquinoline,



This base is obtained by treatment of acetylaminosafrole with phosphoryl chloride under the following simple conditions: The amide (5 grams) was heated with phosphoryl chloride (20 c.c.) until the vigorous reaction set in. This was allowed to end without further heating, and the mixture was then boiled for five minutes. The product was decomposed by water, when all but a small residue remained in the yellow solution. The filtered liquid was basified with ammonia and extracted with ether, and the ethereal solution washed, dried, and evaporated. The residual base could not be induced to crystallise, and was therefore dissolved in acetone (15 c.c.) and mixed with a solution of picric acid (5 grams) in the same solvent (15 c.c.), after which the *picrate*, which crystallised in prisms, was collected and recrystallised from acetone. The canary-yellow substance darkens, when heated, at  $165^{\circ}$ , and then melts and decomposes at  $170^{\circ}$ :

0.2118 gave 22.0 c.c.  $N_2$  at  $15^\circ$  and 758 mm.  $N=13.4$ .

$C_{12}H_{11}O_2N$ ,  $C_6H_5O_2N_3$  requires  $N=13.0$  per cent.

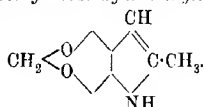
The pure picrate was decomposed by means of aqueous potassium hydroxide in the presence of ether, the ethereal solution being repeatedly washed with dilute alkali in order to remove the last traces of picric acid. The liquid, which exhibited intense green fluorescence, was dried by solid sodium hydroxide, filtered, and the solvent removed by distillation. The pale yellow oil did not crystallise, and after drying in a vacuum gave the following analytical results:

0.1431 gave 0.3733  $CO_2$  and 0.0720  $H_2O$ .  $C=71.1$ ;  $H=5.6$ .

$C_{12}H_{11}O_2N$  requires  $C=71.6$ ;  $H=5.5$  per cent.

This substance had all the chemical properties associated with quinoline derivatives, and condensation reactions similar to those of quinaldine were observed with benzaldehyde and phthalic anhydride. It is not affected by nitrous acid, and its salts, namely, the *sulphate*, *hydrochloride*, and *acetate*, are readily soluble in water. Sparingly soluble precipitates are obtained when its solution in dilute hydrochloric acid is mixed with platinum chloride, mercuric chloride, or concentrated ferric chloride solutions.

5:6-Methylenedioxy-2-methylindole,



6-Acetylaminosaffrole dibromide (10 grams) was boiled with ethyl alcohol (100 c.c.) and potassium hydroxide (40 c.c. of a 50 per cent. aqueous solution) during a quarter of an hour. After dilution with water the substance gradually crystallised from the milky liquid, and was collected and recrystallised from methyl alcohol, and then from light petroleum (b. p.  $50-60^\circ$ ), being so obtained in colourless needles melting at  $152^\circ$ :

0.1218 gave 0.3047  $CO_2$  and 0.0568  $H_2O$ .  $C=68.2$ ;  $H=5.2$ .

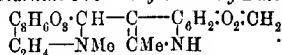
$C_{10}H_9O_2N$  requires  $C=68.6$ ;  $H=5.1$  per cent.

The compound is readily soluble in organic solvents with the exception of light petroleum, in which even when hot it is sparingly soluble. It dissolves in concentrated hydrochloric acid, but the salt is dissociated by water, and the indole derivative is precipitated. In its colour reactions it shows the greatest similarity to 2-methylindole. A pine-shaving in an alcoholic hydrochloric acid solution of the substance acquires an intense crimson colour, and a similar shade is produced in quite dilute acid solution with *p*-dimethyl-



aminobenzaldehyde. The picrate forms intensely red solutions, but consists in the solid state of yellow needles, whilst the benzylidene derivative, prepared analogously to that of 2-methylindole, yields a rosindole on treatment with ferric chloride in alcoholic or acetic acid solution.

*Anhydrocotarnine-5:6-methylenedioxy-2-methylindole,*



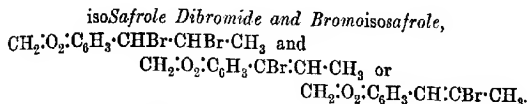
Cotarnine (3 grams) and 5:6-methylenedioxy-2-methylindole (4 grams) were dissolved in ethyl alcohol (15 c.c.), and the mixture allowed to remain overnight. The crystals which had separated were collected and recrystallised from ethyl alcohol, in which the substance is sparingly soluble. The colourless needles melted at 130–135° with evolution of gas, which appeared to be derived from solvent of crystallisation. The substance was again crystallised from benzene, and obtained in satiny needles, which after exposure to a vacuum for several hours melted and decomposed at 207° with previous reddening:

0.1149 gave 0.2832 CO<sub>2</sub> and 0.0584 H<sub>2</sub>O. C=67.2; H=5.7.

C<sub>22</sub>H<sub>20</sub>O<sub>5</sub>N<sub>2</sub> requires C=67.0; H=5.6 per cent.

The substance is readily soluble in benzene, chloroform, or acetone, but sparingly so in alcohol or light petroleum. It yields a sparingly soluble *hydrochloride* and yellow *picrate*, but is readily soluble in dilute aqueous acetic acid, and is recovered unchanged from the cold solution on the addition of ammonia. When, however, the solution of the base in glacial or dilute acetic acid is boiled, cotarninium acetate and 5:6-methylenedioxy-2-methylindole are produced. In cold aqueous alcoholic hydrochloric acid solution no coloration is observed on the addition of *p*-dimethylaminobenzaldehyde, whereas, on warming, the characteristic magenta colour quickly appears, and this reaction must be ascribed to an hydrolysis similar to that which is caused by hot acetic acid. It follows that the active hydrogen atom which is involved in the condensation of the original indole derivative with cotarnine is also that which is responsible for the colour reaction with *p*-dimethylaminobenzaldehyde. Very numerous observations indicate that it is the β-position in the pyrrole ring which is attacked by aldehydes, and we have therefore adopted the constitution shown at the head of the section for our condensation product. Moreover, we have been unable to isolate any definite product resulting from the condensation of cotarnine and 2:3-dimethylindole. Anhydrocotarnine-2-methylindole was prepared by Hope and Robinson (T., 1913, 103, 361), and the opinion was expressed that the cotarnine residue had

become attached to the imino-group. It seems more probable, however, that the constitution of the substance is correctly represented by an expression analogous to that chosen for its methylenedioxy-derivative.

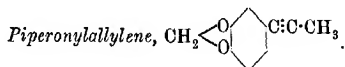


There is some confusion in the literature in regard to the action of bromine on *isosafrole*. We find that bromination in carbon disulphide solution proceeds normally to the dibromide, which on distillation loses a molecule of hydrogen bromide; whilst an excess of bromine in chloroform solution leads to the production of a bromoisosafrole dibromide, which has one of the bromine atoms in the aromatic ring.

*iso*Safrole (10 grams) in carbon disulphide (15 grams) was treated with a solution of bromine in twice its volume of carbon disulphide until the bromine was no longer absorbed. After the removal of the solvent by distillation, the residual oil was washed in ethereal solution with aqueous sodium carbonate, dried, and the ether evaporated, after which the oil was exposed to a vacuum and analysed. A bromine estimation (Found, Br=46.4) showed that the main constituent of this product was *isosafrole* dibromide (Br=49.7 per cent.). This crude dibromide was distilled under diminished pressure, when hydrogen bromide was evolved, and a more mobile oil, *bromoisosafrole*, boiling at 145—150°/15 mm., was obtained:

0.2218 gave 0.1721 AgBr. Br=33.0.

$\text{C}_{10}\text{H}_8\text{O}_2\text{Br}$  requires Br=33.2 per cent.



Monobromoisosafrole (9 grams) was heated during two and a-half hours with methyl alcohol (14 c.c.) and powdered potassium hydroxide (7.5 grams) at 125°. The product, when cold, was poured into water, and the whole extracted with ether. The dried ethereal solution was then distilled, and the following fractions collected: (a) up to 141°, (b) 141°, (c) 141—150°; (b) consisted of the pure acetylene derivative, and crystallised completely, whilst (a) and (c) also yielded crystals, especially when these fractions were cooled in a freezing mixture. The crystals were freed from oily impurities by contact with porous porcelain, and crystallised from light petroleum

(b. p. 50—60°). The substance was obtained in this way in colourless prisms melting at 42—43°:

0.1249 gave 0.3413 CO<sub>2</sub> and 0.0584 H<sub>2</sub>O. C=74.5; H=5.2.

C<sub>10</sub>H<sub>8</sub>O<sub>2</sub> requires C=75.0; H=5.0 per cent.

*Piperonylallylene* is very readily soluble in organic solvents, and dissolves quite readily in boiling light petroleum. It has an odour strongly resembling that of safrole, and is to a small extent volatile in steam. It dissolves in sulphuric acid, yielding an intense purple solution, from which water precipitates a voluminous blue substance. This interesting change is apparently quantitative and simple, but we can offer no suggestion as to the nature of the reaction.

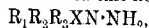
3:4-Methylenedioxypropionophenone, CH<sub>2</sub>:O<sub>2</sub>:C<sub>6</sub>H<sub>3</sub>:CO·CH<sub>2</sub>:CH<sub>3</sub>, which has already been prepared by Wallach and Pond (*Ber.*, 1893, 28, 2719), is readily obtained when piperonylallylene (5 grams) is boiled with ethyl alcohol (60 c.c.), water (60 c.c.), and sulphuric acid (20 c.c.) for three hours. The residue, obtained after extraction with ether and evaporation of the solvent, crystallised after some time. The substance was crystallised from ice-cold alcohol containing a little water, and the satiny needles so obtained melted at 38° (Wallach and Pond, *loc. cit.*, give 39°). The oxide was also prepared and crystallised from ether; it was found to melt, as stated by Wallach and Pond, at 104°.

THE UNIVERSITIES OF MANCHESTER AND SYDNEY.

### CLXXXIII.—*Studies in Substituted Quaternary Azonium Compounds Containing an Asymmetric Nitrogen Atom. Part II. Resolution of Phenylbenzylmethylazonium Iodide into Optically Active Components.*

By BAWA KARTAR SINGH.

IN the present paper the resolution of another enantiomorphous compound the optical activity of which is due to the presence of an asymmetric nitrogen atom is described. The author has already shown (*T.*, 1913, 103, 604) that phenylmethylethylazonium iodide is capable of resolution, but as the value of the molecular rotatory power of the phenylmethylethylazonium ion is low, it was thought that it would be desirable to extend this new series,



y the resolution of other members possessing high rotation constants, thereby also accumulating data connecting constitution with optical rotatory power. With this object the resolution of phenylbenzylmethylazonium iodide was undertaken.

The azonium iodide referred to above was produced in two different ways, namely, by the action of methyl iodide on phenylbenzylhydrazine and of benzyl iodide on phenylmethylhydrazine. The asymmetric azonium iodide was the main product of both the reactions, besides small amounts of by-products which were formed owing to substitution having taken place.

It may be suggested that phenylbenzylmethylazonium iodide may dissociate into the three secondary hydrazines, the formation of which is possible, namely, phenylmethylhydrazine, benzylmethylhydrazine, and phenylbenzylhydrazine, and the corresponding alkyl iodides, and these combinations, in turn, are capable of giving rise to different substituted azonium iodides having two similar radicles, but that in the action of benzyl iodide on phenylmethylhydrazine, under the experimental conditions, benzyldimethylazonium iodide is the only by-product.

Other instances of displacement of alkyl groups similar to the above have been recorded in the cases of the quaternary ammonium compounds (Pope and Read, *T.*, 1912, **101**, 519; Jones, *T.*, 1903, **33**, 1408; 1905, **87**, 1721; and Wedekind, *Ber.*, 1905, **38**, 438), as well as in those of sulphonium compounds (Dehn, *Annalen Suppl.*, **4**, 83).

The thermal decomposition of phenylbenzylmethylazonium hydroxide has also been studied. It is found that in aqueous alcoholic solution the azonium hydroxide decomposes on heating at the temperature of the water-bath into phenylbenzylhydrazine and methyl alcohol. The secondary hydrazine was identified as its hydroferrocyanide, and in this connexion it may be mentioned that a general method for the identification of secondary hydrazines by means of their hydroferrocyanides is developed. These compounds have not hitherto been investigated, and in order to establish their composition they were directly prepared for this purpose.

*Resolution.*—The resolution of phenylbenzylmethylazonium iodide was effected by means of Reyhler's silver *d*-camphor- $\beta$ -sulphonate, and Armstrong and Lowry's silver *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate (*T.*, 1902, **81**, 1441). The hydrogen *d*-tartrate could only be obtained as an oil, which could not be crystallised.

Pope and Read recognised (*T.*, 1910, **97**, 987) that three cases may occur when an externally compensated base is crystallised with an optically active acid: (1) the two salts, *d*B*d*A and *l*B*d*A, crystal-

lise separately, so that each may be readily isolated; (2) a partly racemic compound,  $dB/B, 2dA$ , may be formed, in which case resolution is impossible; (3) each crystal which separates may contain both salts,  $dAdB$  and  $dAlB$ , but in varying proportions; in other words, the two salts form solid solutions one in the other, which can only be partly separated by prolonged fractional crystallisation. Type 3 is well illustrated in the crystallisation of externally compensated sodium 1-methylcyclohexylidene-4-acetate with brucine hydrochloride (Perkin, Pope, and Wallach, T., 1909, **95**, 1790; Pope and Read, T., 1910, **97**, 987), and similar behaviour is met with in the cases of the camphor- $\beta$ -sulphonate and  $\alpha$ -bromocamphor- $\beta$ -sulphonate of phenylbenzylmethylazonium. In the case of the camphorsulphonate, when about one-sixth of the salt  $dAdB$  (melting point  $177^\circ$ ) has separated out in an almost pure condition (see experiment 1, p. 1980), the next fractions exhibit molecular rotatory powers,  $+36.4^\circ$  and  $+28.57^\circ$ ; these, therefore, consist of 43.9 and 40.6 per cent. respectively of  $dAdB$  salt, the rest being made up of the  $lBdA$  component. In the second experiment with the same salt (see p. 1980) about one-eighth of the salt  $dBdA$  separates out in an almost pure condition. The last fractions exhibit molecular rotatory powers,  $+34.5^\circ$  and  $+30.9^\circ$ , and, therefore, consist of the two salts  $dAdB$ ,  $dAlB$ , in the form of their solid solutions one in the other, containing 43 and 41.5 per cent. of the  $dBdA$  component respectively. The points bearing on the lowering of the melting point obtained in experiments 1 and 2 may be considered as follows:

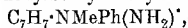
As the amount of the salt  $lBdA$  increases in the solid solution, the melting point falls to  $172$ – $173^\circ$  and  $168$ – $169^\circ$ , having values for  $[M]_D$ ,  $+36.4^\circ$  and  $+34.5^\circ$ , thus containing 43.9 and 43 per cent. of the salt  $dBdA$ . The melting point again rises to  $171^\circ$  with  $[M]_D$ ,  $+28.57^\circ$ , and thus containing 40.6 per cent. of the salt  $dBdA$ . This, therefore, suggests that the eutectic mixture of the two salts above referred to melts in the neighbourhood of  $167$ – $168^\circ$ , and thus consists of about 41.5 per cent. of the salt  $dBdA$  and 58.5 per cent. of  $dBdA$ .

In the case of the bromocamphorsulphonate about one-third of the salt  $dBdA$  separates out in an almost pure condition. The next fractions which are obtained have molecular rotatory powers ranging from  $+247^\circ$  to  $+261^\circ$ . Further crystallisations in different solvents and at lower temperature do not bring about any appreciable resolution. From this it must be concluded that the two component salts have here also formed solid solutions one in the other. The pure  $dBdA$  salt melts at  $197^\circ$ , and as the amount of  $lBdA$  component increases in the solid solution, the melt-

ng point falls to  $175-178^\circ$  with  $[M]_D + 325.1^\circ$ , and thus consisting of about 53.6 per cent. of the salt  $dBdA$  and 46.4 per cent. of the salt  $lBdA$ . The original unresolved salt consisting of 50 per cent. of each component melts at  $173-175^\circ$ . The melting point further falls to  $165-166^\circ$  with  $[M]_D + 261.5^\circ$ , thus consisting of about 21.5 per cent. of the salt  $dBdA$  and 78.5 per cent. of the salt  $lBdA$ . It again rises to  $167-168^\circ$  with  $[M]_D + 253.5^\circ$ , thus corresponding with about 17.4 per cent. of the salt  $dBdA$  and 82.6 per cent. of  $lBdA$ . It follows, from the above, that the eutectic mixture melts in the neighbourhood of  $165-166^\circ$ .

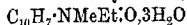
It has been pointed out above that the first fractions of highest melting point represent the  $dBdA$  components in the pure state. This statement is further supported by the fact that the  $d$ -picrates obtained from the camphorsulphonate and the bromocamphor sulphonate give identical values for the molecular rotatory power, thus indicating that complete resolution has taken place in the case of the first fractions. In this connexion it may be pointed out that in view of the difficulties which are experienced in resolving externally compensated compounds, the importance of working with more than one optically active salt for resolution cannot be over-estimated. This need, becomes still more apparent when it is remembered that there is no quantitative relation connecting optical rotation constants with constitution.

The  $d$ - $\beta$ -camphorsulphonate gives the maximum molecular rotatory power for the  $d$ -phenylbenzylmethylazonium ion,



as  $[M]_D$  about  $+119^\circ$  in aqueous solution; the  $d$ - $\alpha$ -bromocamphor- $\beta$ -sulphonate as about  $+99^\circ$ , the  $d$ -iodide as about  $+98^\circ$ , both in methyl alcohol; and the  $d$ -picrate as about  $+89^\circ$  in methyl alcohol, and about  $+254^\circ$  in chloroform solution. These values present a very marked contrast to the maximum rotation constant for the  $l$ -phenylmethylethylazonium ion as  $[M]_D$  about  $-30^\circ$  (*loc. cit.*). It may, therefore, be inferred that the ethyl group has a great inhibiting effect on the value of the rotation constant, and this conclusion becomes strengthened when a similar comparison is made in the case of the quaternary asymmetric ammonium compounds. The ethyl compound of the phenylbenzylmethylammonium series has for the asymmetric ammonium ion  $[M]_D$  about  $+64^\circ$ , the propyl and the isopropyl compounds have  $-299^\circ$  and  $-398^\circ$  respectively. In the phenylmethylallylammonium series the ethyl compound gives for the basic ion,  $[M]_D + 16^\circ$ , and the  $n$ -propyl and the isopropyl compounds give  $[M]_D + 106^\circ$  and  $-103^\circ$  respectively. Yet in another class of compounds, namely, those investigated by Meisenheimer, the value of  $[M]_D$  for hydroxyphenylmethylethylammonium

chloride,  $\text{OH}\cdot\text{NMeEtPhCl}$  (*Ber.*, 1908, **41**, 3966), and for hydroxy- $\beta$ -naphthylmethylethylammonium hydroxide,



(*Annalen*, 1911, **385**, 117) is only  $41^\circ$  and  $39^\circ$  respectively. The above comparison clearly points to a constitutive effect, which is conditioned to some extent at least by the presence of an ethyl group in the molecule.

No mutarotation has been observed in the case of the compounds described in the present paper, either on keeping or on heating their solutions. This is the more remarkable as solutions of the salts of phenylmethylethylazonium undergo inversion on keeping (*loc. cit.*). The influence of solvents on the rotation constants of phenylbenzylmethylazonium salts is very marked. The molecular rotatory power is almost three times as great in chloroform as in methyl alcohol or acetone.

The *dl*-salts have, in all the cases examined, higher melting points than the corresponding *d*-salts. It may, therefore, be concluded that they are not *dl*-mixtures (conglomerates), although the question as to whether they are racemic compounds or pseudo-racemic mixed crystals is left open.

#### EXPERIMENTAL.

##### *Phenylbenzylmethylazonium Iodide*, $\text{C}_7\text{H}_7\cdot\text{NMePhI}\cdot\text{NH}_2$ .

This substance was prepared by two different methods:

(a) *By the Action of Methyl Iodide on Phenylbenzylhydrazine*.—Phenylbenzylhydrazine (20 grams) was mixed with one molecular proportion of methyl iodide (15 grams) in the presence of a little ether; the mixture was cooled in ice, and the white, crystalline substance which separated overnight (10.2 grams), on recrystallisation from hot alcohol, melted and decomposed at  $122^\circ$ .

The mother liquor, on keeping for ten days, deposited a very small quantity of a crystalline material (about 0.2 gram), which after recrystallisation from alcohol and ether melted and decomposed at  $186$ – $187^\circ$ :

0.2077 gave 0.1857 AgI.  $I=48.31$ .

The substance cannot be phenyldimethylazonium iodide (which requires  $I=48.1$  per cent.), for the latter melts and decomposes at  $126$ – $127^\circ$ , as is shown below.

(b) *By the Action of Benzyl Iodide on Phenylmethylhydrazine*.—An ice-cold ethereal solution of phenylmethylhydrazine (25 grams) was added to one molecular proportion of an ethereal solution of benzyl iodide (45 grams), also cooled in ice. The crude product (34.5 grams), after recrystallisation from hot alcohol, melted and decomposed at  $122^\circ$ . The azonium iodide turns red a few degrees

below its melting point. A mixture of the azonium iodide obtained by the two different methods gave the same melting point; the second method of preparation gave much the better yield. It is soluble in methyl alcohol or acetone, less so in ethyl alcohol or chloroform, very sparingly so in cold water, and insoluble in benzene or ether:

0.3837 gave 0.2650 AgI.  $I=37.32$ .

0.2189 „ 0.3990  $\text{CO}_2$ , 0.1077  $\text{H}_2\text{O}$ , and 0.0816 I (by Drenstedt's method).  $C=49.7$ ;  $H=5.44$ ;  $I=37.28$ .

$\text{C}_{14}\text{H}_{17}\text{N}_2\text{I}$  requires  $C=49.4$ ;  $H=5.0$ ;  $I=37.35$  per cent.

It may be pointed out that the cooling and dilution of the reaction mixture with ether are both essential for the formation of the quaternary azonium iodide. If they are omitted, the reaction becomes very violent owing to rise of temperature with copious evolution of irritating vapours of benzyl iodide. Only a dark, tarry product remains behind, from which no crystalline substance can be isolated.

The mother liquor from the action of benzyl iodide on phenylmethylhydrazine yielded a small, crystalline crop (2.3 grams) of higher melting point. It was recrystallised three times from hot alcohol, and melted and decomposed at  $125^\circ$ . This salt does not turn red below its melting point, but only acquires a yellow colour:

0.1359 gave 0.1947  $\text{CO}_2$  and 0.0680  $\text{H}_2\text{O}$ .  $C=39.07$ ;  $H=5.56$ .

0.1165 „ 9.9 c.c.  $\text{N}_2$  (moist) at  $27^\circ$  and 761.6 mm.  $N=9.45$ .

0.1750 „ 0.1479 AgI.  $I=45.67$ .

$\text{C}_9\text{H}_{10}\text{N}_2\text{I}$  requires  $C=38.84$ ;  $H=5.4$ ;  $N=10.07$ ;  $I=45.61$  per cent.

The above analytical data agree with those for *benzyl dimethylazonium iodide*.

*dl-Phenylbenzylmethylazonium chloride* crystallises in thin, colourless prisms, which melt and decompose at  $158-159^\circ$ . It is very readily soluble in water or alcohol, but insoluble in benzene or ether:

0.39655 gave 0.23015 AgCl.  $\text{Cl}=14.36$ .

$\text{C}_{14}\text{H}_{17}\text{N}_2\text{Cl}$  requires  $\text{Cl}=14.28$  per cent.

The corresponding *platinichloride* crystallises from boiling water acidified with hydrochloric acid in orange-coloured needles melting and decomposing at  $162^\circ$ . It is insoluble in cold water, as well as in organic solvents, but dissolves in much boiling water:

0.2182 gave 0.0507 Pt.  $\text{Pt}=23.23$ .

$(\text{C}_{14}\text{H}_{17}\text{N}_2)_2\text{PtCl}_6$  requires  $\text{Pt}=23.40$  per cent.

The *aurichloride* is almost insoluble in cold water, but dissolves in boiling water, from which solvent, in the presence of hydrochloric



acid, it separates in yellow, stout prisms, melting and decomposing at  $134^{\circ}$ :

0.2151 gave 0.07715 Au. Au=35.87.

$C_{14}H_{17}N_2AuCl_4$  requires Au=35.71 per cent.

The *hydroferrocyanide*,  $(C_7H_7 \cdot NMePh \cdot NH_2)_3 \cdot H_5Fe(CN)_{12}$ , is almost insoluble in water or organic solvents, and is obtained as a white precipitate by mixing aqueous solutions of potassium ferrocyanide and the azonium chloride in the presence of a mineral acid. It does not melt, but decomposes gradually on heating. In composition it corresponds with an acid salt:

0.3404 gave 0.0531  $Fe_2O_3$ . Fe=10.9.

$C_{34}H_{56}N_{18}Fe$  requires Fe=10.46 per cent.

The *hydroferricyanide*,  $(C_7H_7 \cdot NMePh \cdot NH_2)_2 \cdot HFe(CN)_6$ , is soluble in water or methyl alcohol, insoluble in chloroform or ether, and crystallises in yellow prisms, which melt and decompose at  $140^{\circ}$ . In composition it also corresponds with an acid salt:

0.3006 gave 0.0379  $Fe_2O_3$ . Fe=8.81.

0.0684 „ 12.9 c.c.  $N_2$  (moist) at  $23.5^{\circ}$  and 763 mm. N=21.29.

$C_{34}H_{55}N_{10}Fe$  requires Fe=8.74; N=21.92 per cent.

$C_{34}H_{55}N_{10}Fe \cdot H_2O$  requires Fe=8.5; N=21.31 per cent.

As the salt, on keeping in the steam-oven, undergoes decomposition with change of colour, its water of crystallisation could not be directly determined.

#### dl-Phenylbenzylmethyazonium Mercuri-iodides.

I.  $(C_7H_7 \cdot NMePh \cdot NH_2)_2 \cdot HgI_2$ , prepared from the azonium iodide and mercuric iodide (one-half molecular proportion), crystallises from methyl alcohol in colourless prisms, melting and decomposing at  $135-136^{\circ}$  to a green liquid. It is very readily soluble in acetone, moderately so in methyl alcohol, sparingly so in cold alcohol, but more so in hot, and is insoluble in ether or water:

0.2765 gave 11.65 c.c.  $N_2$  (moist) at  $22^{\circ}$  and 765.6 mm. N=4.81.

$C_{28}H_{34}N_4I_2Hg$  requires N=4.94 per cent.

II.  $C_7H_7 \cdot NMePh \cdot NH_2 \cdot HgI_2$ , prepared from one molecular proportion of mercuric iodide, separates from alcohol in yellow prisms, melting and decomposing at  $128-129^{\circ}$  to a green liquid. It is very readily soluble in acetone or methyl alcohol, sparingly so in ethyl alcohol, and insoluble in ether, chloroform, or water:

0.1725 gave 5.6 c.c.  $N_2$  (moist) at  $24^{\circ}$  and 762.8 mm. N=3.66.

$C_{14}H_{17}N_2I_2Hg$  requires N=3.53 per cent.

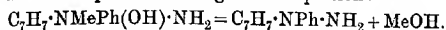
The *dl-picrate*,  $C_7H_7 \cdot NMePh(NH_2) \cdot O \cdot C_6H_3O_2N_3$ , crystallises from alcohol in yellow prisms, melting and decomposing at  $152^{\circ}$ . It is very readily soluble in acetone, moderately so in methyl alcohol,

somewhat less so in cold alcohol or chloroform, but more so in hot; it is insoluble in ether or water:

0.0920 gave 12.8 c.c.  $N_2$  (moist) at  $23.5^\circ$  and 763.5 mm.  $N=15.72$ .

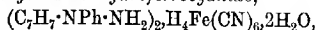
$C_{20}H_{19}O_7N_5$  requires  $N=15.87$  per cent.

The *azonium hydroxide*,  $C_7H_7 \cdot NMePh(OH) \cdot NH_2$ , is strongly alkaline, and can only be obtained as a syrup. Its alcoholic solution, on being heated on the water-bath for some time, becomes turbid, and decomposes according to the equation:



Contrary to expectation, the methyl group is eliminated, and the heavier benzyl radicle remains attached to the nitrogen atom. The secondary hydrazine was identified as its hydroferrocyanide (Found,  $Fe=8.63$ ;  $N=21.50$ . Calc.,  $Fe=8.61$ ;  $N=21.61$  per cent.).

*Phenylbenzylhydrazine hydroferrocyanide*,



separates as an amorphous, white precipitate by mixing an aqueous solution of potassium ferrocyanide with an acidified solution of phenylbenzylhydrazine. It is insoluble in water, but dissolves in alcohol. It does not melt, but begins to decompose gradually on heating:

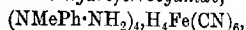
0.2830 gave 0.0347  $Fe_2O_3$ .  $Fe=8.57$ .

0.0831 „ 15.5 c.c.  $N_2$  (moist) at  $21^\circ$  and 766 mm.  $N=21.41$ .

$C_{32}H_{32}N_{10}Fe, 2H_2O$  requires  $Fe=8.61$ ;  $N=21.61$  per cent.

As the salt undergoes decomposition in the steam-oven, its water of crystallisation could not be determined, but analyses show that it contains  $2H_2O$ .

*Phenylmethylhydrazine hydroferrocyanide*,



is similarly obtained in colourless prisms. It is soluble in cold water, but less so in alcohol.

It does not melt, but decomposes on heating:

0.3030 gave 0.0355  $Fe_2O_3$ .  $Fe=8.19$ .

0.1686 „ 0.0192  $Fe_2O_3$ .  $Fe=7.96$ .

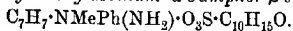
0.0836 „ 19.5 c.c.  $N_2$  (moist) at  $19^\circ$  and 771.5 mm.  $N=27.22$ .

0.0794 „ 18.8 c.c.  $N_2$  (moist) at  $21^\circ$  and 769.7 mm.  $N=27.31$ .

$C_{34}H_{44}N_{14}Fe$  requires  $Fe=7.93$ ;  $N=27.85$  per cent.

$C_{34}H_{44}N_{14}Fe, 1H_2O$  requires  $Fe=7.73$ ;  $N=27.15$  per cent.

*Phenylbenzylmethylazonium d-Camphor- $\beta$ -sulphonate*,



Finely powdered phenylbenzylmethylazonium iodide (30.5 grams) was added in small quantities at a time to one molecular proportion of silver *d*-camphor- $\beta$ -sulphonate dissolved in boiling ethyl acetate

moistened with a few drops of water, on the water-bath. The contents of the flask were kept shaken, and after the addition of the whole of the azonium iodide, the heating was continued for some time to complete the reaction. The ethyl acetate was distilled off, and the residue consisting of the azonium camphorsulphonate and silver iodide was extracted with methyl alcohol until only silver iodide remained behind. The camphorsulphonate obtained in this way melted at 170—171°. It is very readily soluble in methyl alcohol or chloroform, moderately so in alcohol or water, sparingly so in benzene, but insoluble in ether:

0.1063 gave 0.2537 CO<sub>2</sub> and 0.0707 H<sub>2</sub>O. C=65.09; H=7.39.

C<sub>24</sub>H<sub>32</sub>O<sub>4</sub>N<sub>2</sub>S requires C=64.86; H=7.21 per cent.

The above camphorsulphonate was subjected to fractional crystallisation by dissolving it in the least possible quantity of cold methyl alcohol, and precipitating by gradual addition of ether.

Experiment I was conducted with 12 grams of the substance melting at 170—171°:

Fraction.	Yield in grams.	M. p.	Substance taken in grams.	$n_D$	$[\alpha]_D^*$	$[M]_D$
A .....	2.1	175—176°	0.4383	+1.61°	+36.55°	+162.3°
B .....	2.0	172—173	0.2790	0.23	8.2	36.4
C .....	4.0	171°	0.2629	0.17	6.43	28.57

Fraction A was subjected to further crystallisations in the same way with the following results:

	$n_D$	$[\alpha]_D$	$[M]_D$
2nd recrystallisation—m. p. 176°; 0.2931 gram of substance .....	+1.03°	+34.8°	+154.5°
After 68 hours .....	1.07	36.5	162.06
3rd recrystallisation—m. p. 176°; 0.3759 gram of substance .....	1.37	36.2	161.3
After 4 hours .....	1.38	36.56	162.3
4th recrystallisation—m. p. 176—177°; 0.3455 gram of substance .....	1.26	36.3	161.2
After 96 hours .....	1.25	36.0	159.9

The rotatory power was determined in water at 29—30°.

Experiment II was similarly made with 19 grams of salt having  $[M]_D + 66.9^\circ$ :

Fraction.	Yield in grams.	M. p.	Substance taken in grams.	$n_D$	$[\alpha]_D$	$[M]_D$
I. ....	3.2	174—175°	0.1861	+0.56°	29.95°	133.0°
II. ....	2.1	172—174	0.2669	0.35	13.06	57.95
III. ....	10.0	167—168	0.1572	0.11	6.96	30.9
IV. ....	1.4	168—169	0.2334	0.18	7.67	34.5

\* The given weight of the substance was dissolved in 19.9 c.c. of the solvent and the rotatory power determination was made in a 2-dm. tube about thirty minutes after solution. This applies to all observations recorded in this paper unless the contrary is stated.

Fraction I was further submitted to fractional crystallisation with the following result:

	$\alpha_D$	$[\alpha]_D$	$[M]_D$
1st crystallisation—m. p. 175—176°; 0.2297 gram of substance	+0.84°	+36.4°	+161.6°
After 16 hours	0.81	35.1	155.8
2nd crystallisation—m. p. 177°; 0.1037 gram of substance	0.40	38.4	170.5
After 26 hours	0.40	38.4	170.5

The value of  $[M]_D$  was not raised by further crystallisation. The fraction melting at 176—177°, and having  $[M]_D + 170^\circ$  represents, therefore, the pure *d*-phenylbenzylmethylazonium *d*-camphor- $\beta$ -sulphonate.

The rotatory power was determined in water at 29—30°.

Fractions III and IV from the second experiment, and B and C from the first experiment, which amounted to about 17 grams, were mixed together, and had  $[M]_D$  ranging from +29° to +36°. These fractions, which contained an excess of the salt of the *l*-*iso*-component of the base, were subjected to a prolonged process of fractional crystallisation, but without any success at further resolution:

	$\alpha_D$	$[\alpha]_D$	$[M]_D$
1st recrystallisation—m. p. 167—169°; 0.3474 gram of substance	+0.285°	+8.16°	+36.25°
After 6 hours	0.29	8.3	36.9
2nd recrystallisation—m. p. 170—171°; 0.2235 gram of substance	0.17	7.57	33.6
Last fraction (mother liquor)—0.1764 gram of substance	0.16	9.02	40.07

The last value refers to the solid obtained from the mother liquor by evaporating it to dryness in a vacuum desiccator. One more recrystallisation from chloroform and ether gave the following value:

	$\alpha_D$	$[\alpha]_D$	$[M]_D$
0.2132 gram of substance	+0.18°	+8.44°	+37.49°

It was further recrystallised from acetone and ether, with the following result:

	$\alpha_D$	$[\alpha]_D$	$[M]_D$
0.4713 gram of substance	+0.37°	+7.81°	+34.66°

The rotatory power was determined in water at 29—30°.

The *l*-iodide, which was precipitated in colourless prisms from an aqueous solution of the last fraction of the camphorsulphonate by means of potassium iodide, melted and decomposed at 123—124°. Its rotatory power was determined with the following result:

0.1222 in 19.9 c.c. of methyl alcohol gave  $\alpha_D - 0.04^\circ$ , whence  $[\alpha]_D - 3.25^\circ$  and  $[M]_D - 11.1^\circ$ .

*dl*-Phenylbenzylmethylazonium *d*- $\alpha$ -Bromocamphor- $\beta$ -sulphonate,  
 $C_7H_7 \cdot NMePh(NH_2) \cdot O_3S \cdot C_{10}H_{14}OBr$ .

This salt was prepared from the azonium iodide, and the silver salt of Armstrong and Lowry's *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonic acid in the same way as the above-described azonium camphorsulphonate. The bromocamphorsulphonate, obtained in this way, melted at 173–175°; the yield was almost theoretical:

0.1524 gave 0.3052 CO<sub>2</sub> and 0.0861 H<sub>2</sub>O. C=54.6; H=6.28.

C<sub>24</sub>H<sub>31</sub>O<sub>4</sub>N<sub>2</sub>BrS requires C=55.06; H=5.93 per cent.

*d*-Phenylbenzylmethylazonium *d*- $\alpha$ -Bromocamphor- $\beta$ -sulphonate.

The bromocamphorsulphonate (25 grams), as obtained in the above way, was subjected to fractional crystallisations as follows:

It was dissolved in the least possible quantity of methyl alcohol, and precipitated by the addition of successive quantities of ether.

Fraction.	Yield in grams.	M. p.	Substance taken in grams.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Original unresolved salt .....	—	173–175°	0.1051	+ 0.643°	+ 60.89°	+ 318.84°
I. ....	8.9	195°	0.1829	1.45	78.9	412.6
II. ....	6.9	175–178	0.1180	0.737	62.16	325.1
III. ....	2.7	165–166	0.1054	0.50	47.22	247.0

The rotatory power was determined in methyl alcohol at 25°.

Fraction II yielded 2 grams of almost pure *dAdB* salt (melting at 196°), which was added to fraction I, and also 3 grams of salt melting at 167–168° added to fraction III.

Fraction I (10.9 grams) was further subjected to a similar process of fractional crystallisation, and its rotatory power was determined in methyl alcohol with the following result:

	Temperature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
2nd recrystallisation—m. p. 196–197°;				
0.2657 gram of substance .....	23°	+ 2.115°	+ 79.23°	+ 414.4°
After 19 hours .....	23	2.13	79.77	417.3
3rd crystallisation—m. p. 196–197°;				
0.1445 gram of substance .....	23	1.12	77.11	403.11
4th recrystallisation—m. p. 197°; 0.1111				
gram of substance .....	24	0.873	78.6	411.8
After 46 hours .....	25	0.86	77.41	404.8
0.1215 gram of substance (19.9 c.c. of				
chloroform) .....	28	1.057	86.58	452.8
After 20 hours .....	26	1.075	88.06	460.5

The fraction melting at 197° represents, therefore, the pure *d*-phenylbenzylmethylazonium *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate. It is moderately soluble in methyl alcohol or water, but insoluble in ether or benzene:

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0.1800 gave 0.3641 CO<sub>2</sub> and 0.0946 H<sub>2</sub>O. C=55.15; H=5.84.

C<sub>24</sub>H<sub>31</sub>O<sub>4</sub>N<sub>2</sub>BrS requires C=55.06; H=5.93 per cent.

*1-Phenylbenzylmethyazonium d-α-Bromocamphor-β-sulphonate.*

This salt is left behind in the mother liquor: it could not be obtained in a pure state, as is evident from a determination of its rotatory power.

Fraction III (5.7 grams) was subjected to a prolonged process of fractional crystallisations with the following results:

	Tempera- ture.	$\alpha_D$	$[\alpha]_D$	$[M]_D$
2nd crystallisation—m. p. 167—168°; 0.0678 gram of substance .....	24°	+ 0.33°	+ 48.45°	+ 253.5°
3rd crystallisation—m. p. 165—166°; 0.0866 gram of substance .....	26.5	0.435	49.99	261.5
4th crystallisation—m. p. 166—167°; 0.1222 gram of substance .....	26.5	0.60	48.86	255.5
5th crystallisation—m. p. 165—166°; 0.1179 gram of substance .....	27	0.585	49.38	258.2

It is evident from the slow resolution that the two salts *dAdB* and *dAB* have formed solid solutions one in the other; other solvents like chloroform or acetone and the lower temperature of melting ice were employed for fractional crystallisation, but no further resolution took place. The rotation constants indicate that the above fractions consist of about 19 per cent. of salt *dBdA* and 31 per cent. of *iBdA*. The salt is very readily soluble in methyl alcohol, acetone, or chloroform, less so in ethyl alcohol or water, and insoluble in ether:

0.1172 gave 0.2382 CO<sub>2</sub> and 0.0666 H<sub>2</sub>O. C=55.42; H=6.31.

C<sub>24</sub>H<sub>31</sub>O<sub>4</sub>N<sub>2</sub>BrS requires C=55.06; H=5.93 per cent.

*d-Phenylbenzylmethyazonium Iodide*, C<sub>7</sub>H<sub>7</sub>·NMePhI·NH<sub>2</sub>.

The active iodide was precipitated in white prisms on the addition of a concentrated solution of potassium iodide to an aqueous solution of the camphorsulphonate (m. p. 177° and  $[M]_D$  + 170.5°); it melted and decomposed at 114°.

Determination of the rotatory power at 28° gave the following result in methyl alcohol:

	$\alpha_D$	$[\alpha]_D$	$[M]_D$
0.2022 gram of substance.			
After 20 minutes .....	- 0.587°	+ 28.89°	+ 98.22°
After 9 hours .....	0.54	26.58	90.37
After 25 hours .....	0.49	24.12	82.0
After 53½ hours .....	0.513	25.35	85.83

At the time of the last observation the solution in the tube had acquired a yellow colour, probably owing to decomposition. The chloroform solution of the active iodide acquired a deep yellow

colour, and had thus practically cut off most of the light. For this reason the value of the rotation constant was untrustworthy except in indicating that it was much higher than that in methyl alcohol.

*d*-Phenylbenzylmethylazonium Picrate,  
 $C_7H_7 \cdot NMePh(NH_2) \cdot O \cdot C_6H_4O_6N_3$ .

The active picrate was prepared by adding a methyl-alcoholic solution of the camphorsulphonate or the bromocamphorsulphonate of the *d*-base to a methyl-alcoholic solution of picric acid. On concentrating the solution, yellow prisms separated, which after one or more crystallisations from alcohol and ether melted and decomposed at 146—147°. The externally-compensated picrate melts at a higher temperature, namely, 152°:

0.0445 gave 6.2 c.c.  $N_2$  (moist) at 20° and 762.5 mm.  $N = 15.99$ .

$C_{20}H_{19}O_7N_3$  requires  $N = 15.87$  per cent.

The rotatory-power determination made with a sample prepared from the camphorsulphonate gave the following value:

0.1055 gram of substance (in methyl alcohol).	Tempera- ture.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	25°	+0.215°	+20.27°	+89.35°
After 20 hours .....	25	0.214	20.19	88.95

The solution was heated to boiling for half-an-hour under reflux, but the rotatory power remained unaltered:

0.0415 gram of substance (in chloroform).	Tempera- ture.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	21.5°	+0.24	+57.55°	+253.8°
After 80 hours .....	23	0.23	56.14	243.1

The optical rotatory-power determination made with a sample prepared from the bromocamphorsulphonate gave the following value:

0.0818 gram of substance in 19.9 c.c. of methyl alcohol	Tempera- ture.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	26°	+0.16°	+19.86°	+87.59°
After 24 hours .....	26	0.157	19.1	84.22

0.0759 gram of substance in 20.25 c.c. of chloroform	Tempera- ture.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	26.5°	+0.427°	+56.98°	+251.25°
After 13½ hours .....	24	0.428	57.11	251.8
After 36 hours .....	25	0.43	57.38	253.1

The above agreement in the value of the rotatory power of the picrate as obtained from the two different salts indicates that the salt *d*A/B is the pure component. The value of the rotation constant is about three times as large in chloroform as in methyl alcohol.

*l*-Phenylbenzylmethyazonium Picrate.

This substance, obtained from the bromocamphorsulphonate of the *l*-base, in the same way as its enantiomorphously related isomeride, melts and decomposes at  $146^{\circ}$ , and is very readily soluble in acetone or methyl alcohol, less so in chloroform, and insoluble in ether or water:

0.1015 gave 13.8 c.c.  $N_2$  (moist) at  $24^{\circ}$  and 763.4 mm.  $N = 15.32$ .

$C_{20}H_{19}O_7N_3$  requires  $N = 15.87$  per cent.

The rotatory-power determination gave the following result:

0.1252 gram in methyl alcohol.	Temperature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	$28^{\circ}$	$-0.18^{\circ}$	$-14.31^{\circ}$	$-63.09^{\circ}$
After 25 hours .....	26	0.18	14.31	63.09
0.902 gram in chloroform				
After half an hour .....	$25^{\circ}$	$-0.39^{\circ}$	$-43.03^{\circ}$	$-189.7^{\circ}$
After 65 hours .....	24	0.38	41.93	184.9

The rotation constants indicate that about 14 per cent. of the *l*-picrate is present in combination with the *l*-picrate.

*d*-Phenylbenzylmethyazonium Mercuri-iodides.

I.  $(C_7H_7 \cdot NMePhI \cdot NH_2)_2 \cdot HgI_2$ , obtained from the bromocamphorsulphonate of the *d*-base, resembles the externally compensated salt, and melts and decomposes at  $128-129^{\circ}$ :

0.1868 gave 8.2 c.c.  $N_2$  (moist) at  $23^{\circ}$  and 765.7 mm.  $N = 4.99$ .

$C_{28}H_{34}N_4I_4Hg$  requires  $N = 4.94$  per cent.

The following rotatory-power determination was made in acetone:

0.2364 gram of substance.	Temperature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	$26^{\circ}$	$+0.38^{\circ}$	$+16.0^{\circ}$	$+181.4^{\circ}$
After 96 hours .....	28	0.26	10.94	124.1

At the time of the last observation the solution had acquired a deep yellow colour. The lower value is due to the solution having undergone decomposition. The above rotation constant gives  $90.7^{\circ}$  as the molecular rotatory power for the single phenylbenzylmethyazonium ion.

II.  $C_7H_7 \cdot NMePhI \cdot NH_2 \cdot HgI_2$  resembles the externally compensated isomeride, but melts and decomposes at  $124^{\circ}$  to a green liquid:

0.2312 gave 7.55 c.c.  $N_2$  (moist) at  $23^{\circ}$  and 765 mm.  $N = 3.7$ .

$C_{14}H_{17}N_3I_2Hg$  requires  $N = 3.53$  per cent.

The following rotatory-power determination was made in acetone:

0.1437 gram of substance.	Temperature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
After half an hour .....	$26^{\circ}$	$+0.16^{\circ}$	$+11.08^{\circ}$	$+87.99^{\circ}$
After 74 hours .....	26	0.16	11.08	87.99



The *d-platinichloride* resembles the externally-compensated salt, but melts and decomposes at  $154^{\circ}$ :

0.2268 gave 0.0534 Pt. Pt = 23.54.

$(C_{11}H_{17}N_2)_2PtCl_6$  requires Pt = 23.40 per cent.

As the substance is insoluble, its rotatory power could not be determined. There is no doubt, however, that the substance is active, as it melts like other optically active salts, described in this paper, at a lower temperature than the externally-compensated *platinichloride*.

The *d-aurichloride* is readily soluble in methyl and ethyl alcohols, sparingly so in chloroform, and insoluble in ether or water; it melts at  $123-129^{\circ}$ :

0.3269 gave 0.1168 Au. Au = 35.73.

$C_{11}H_{17}N_2AuCl_4$  requires Au = 35.71 per cent.

The following rotatory-power determination was made in methyl alcohol solution:

0.1237 gram of substance.	Temperature.	$\alpha_D$ .	$[\alpha]_{20}$ .	$[M]_D$ .
After half an hour .....	$24.5^{\circ}$	$+0.18^{\circ}$	$+14.48^{\circ}$	$+79.92$
After 29 hours .....	$24.5$	$0.19$	$15.28$	$84.34$

#### *Phenyldibenzylazonium Iodide*, $NPh(C_7H_7)_2I \cdot NH_2$ .

Phenylbenzylhydrazine (16 grams) was treated with one molecular proportion of a cooled solution of benzyl iodide (18 grams) in ether. The crude product (18.7 grams) on being recrystallised from hot alcohol, melted and decomposed at  $133-134^{\circ}$ . It is soluble in hot alcohol, very sparingly so in water, and insoluble in ether:

0.3034 gave 0.1695 AgI. I = 30.19.

$C_{20}H_{21}N_2I$  requires I = 30.53 per cent.

The *aurichloride* is insoluble in water, but dissolves in hot methyl alcohol, and crystallises from the latter solvent in long, yellow prisms, melting and decomposing at  $147-148^{\circ}$ :

0.2406 gave 0.07535 Au. Au = 31.32.

$C_{20}H_{21}N_2AuCl_4$  requires Au = 31.40 per cent.

The *platinichloride* is insoluble in water or cold alcohol, but crystallises from hot alcohol in very fine, buff-coloured needles, melting and decomposing at  $151^{\circ}$ :

0.2184 gave 0.0435 Pt. Pt = 19.91.

$(C_{20}H_{21}N_2)_2PtCl_6$  requires Pt = 19.77 per cent.

#### *Phenyldimethylazonium Iodide*, $NMe_2PhI \cdot NH_2$ .

Phenylmethylhydrazine (12.2 grams) was mixed with one molecular proportion of methyl iodide (15 grams) in ethereal solution

the cold. The crude product (22 grams), after recrystallisation, separates in colourless, stout prisms, melting and decomposing at  $26^{\circ}$ . It is very readily soluble in methyl alcohol, moderately so in water, sparingly so in alcohol, and insoluble in chloroform, ether, or benzene:

0.18305 gave 0.1624 AgI.  $I=47.94$ .

0.2099 „ 0.2817  $\text{CO}_2$ , 0.1011  $\text{H}_2\text{O}$ , and 0.1004 l.  $C=36.6$ ;  
 $H=5.35$ ;  $I=47.83$ .

$\text{C}_8\text{H}_{13}\text{N}_2\text{I}$  requires  $C=36.37$ ;  $H=4.92$ ;  $I=48.11$  per cent.

The *azonium chloride* is readily soluble in alcohol and water, and is very hygroscopic; it melts and decomposes at  $187-188^{\circ}$ :

0.1822 gave 0.1509 AgCl.  $\text{Cl}=20.49$ .

$\text{C}_8\text{H}_{13}\text{N}_2\text{Cl}$  requires  $\text{Cl}=20.58$  per cent.

The *platinchloride* crystallises from hot water in yellow prisms, melting and decomposing at  $158-159^{\circ}$ ; it is sparingly soluble in cold water, and insoluble in alcohol:

0.2463 gave 0.07035 Pt.  $\text{Pt}=28.57$ .

$(\text{C}_8\text{H}_{13}\text{N}_2)_2\text{PtCl}_6$  requires  $\text{Pt}=28.60$  per cent.

The *aurichloride* is soluble in alcohol, sparingly so in cold water, and crystallises from hot water in minute, yellow prisms, melting and decomposing at  $123-124^{\circ}$ :

0.25405 gave 0.1051 Au.  $\text{Au}=41.37$ .

$\text{C}_8\text{H}_{13}\text{N}_2\text{AuCl}_4$  requires  $\text{Au}=41.41$  per cent.

The author desires to express his gratitude to Prof. W. J. Pope, F.R.S., for his kindness in reading this paper in manuscript form, and his appreciation of the friendly interest of his colleague, Dr. L. R. Watson.

Further work with other members of the azonium series is in progress.

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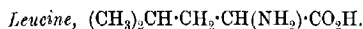
CLXXXIV.—*The Influence of Acids and Alkalis on the Optical Activity of Some Amino-acids.*

By JOHN KERFOOT WOOD.

THE results of the large amount of work done during recent years on amphoteric electrolytes have led to the view that in aqueous solutions of such substances there is formed, as a result of the neutralisation of the basic and acidic groups of the compound, a kind of internal salt. Assuming such a constitution to be correct, it appeared to the author that in the case of optically active amphoteric compounds like some of the amino-acids it might be possible to arrive at some knowledge as to the acid and basic strength of the compounds by an adaptation of the polarimetric-avidity method described by Walker (*Zeitsch. physikal. Chem.*, 1903, **46**, 30). With this object in view, determinations have been made of the optical activity of several amino-acids both in aqueous solution and in the presence of varying amounts of acids and of alkali. It soon became evident that a method of this description would be incapable of application to optically active amino-acids in general, because of the very sparing solubility of many such substances in water, and the consequent difficulty of obtaining trustworthy values for the specific rotation, not only in purely aqueous solution, but also in those cases where the quantity of acid or alkali added was insufficient to form an external salt with the amphoteric compound. It has been possible, however, to carry out such experiments with leucine, aspartic acid, and glutamic acid, the results obtained being given in the present paper. Experiments of the above-mentioned character were carried out by Becker (*Ber.*, 1881, **14**, 1028), both with aspartic acid and asparagine, but the subsequent work of Cook (*Ber.*, 1897, **30**, 296) and Fischer (*Ber.*, 1899, **32**, 2462) has shown the inaccuracy of some of his values for the former substance, so that it became necessary to repeat many of his experiments. It may be here mentioned that, apart from the difference in magnitude of the values obtained, similar results were arrived at by Becker and the author as to the influence exerted by varying amounts of hydrochloric acid on the optical activity of aspartic acid.

In the determination of the optical activity of the various solutions, a Schmidt and Haensch polarimeter (triple field) was employed. All determinations were made at 25°, water from a thermostat being kept in constant circulation through the jacket of the polarimeter tube; a 2-dm. tube was used throughout. The

majority of the solutions employed had a concentration of from 1 to 2 per cent., but in some of the solutions of aspartic acid, owing to the sparing solubility of the substance, more dilute solutions had to be used. The use of dilute solutions certainly increases the difficulty of obtaining accurate values for the specific rotation, but a truer comparison of the results given by the various solutions can be made when these solutions contain approximately equal amounts of the amphoteric compound. Moreover, by using dilute solutions, the salts present may be taken as being almost completely ionised, and the values for the specific rotation will therefore correspond with this condition of the salts.



An aqueous solution of this substance gave the value for the specific rotation as  $[\alpha]_D -9.84^\circ$ .

The effect of varying quantities of hydrogen chloride on the specific rotation is shown in the following table:

Molecules of hydrogen chloride/ molecules of leucine.	$[\alpha]_D$	Molecules of hydrogen chloride/ molecules of leucine.	$[\alpha]_D$
0.55	1.70°	2.82	11.23°
0.87	6.50	5.11	12.14
1.06	7.83	7.51	11.39
1.34	11.20	8.62	12.88
2.21	12.56		

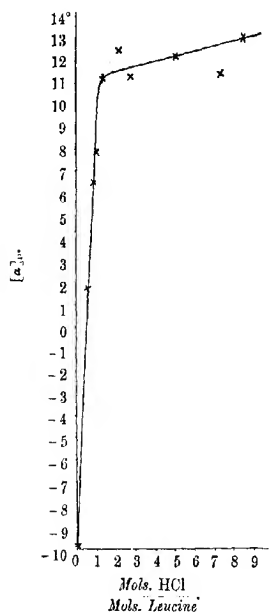
It is evident that as the ratio of hydrogen chloride to leucine is increased there is, at first, a marked change in the optical activity of the solution, but that when the molecular ratio reaches a value between one and two the further addition of hydrogen chloride causes little further change in the specific rotation; this is shown in Fig. 1.

The following table shows the results obtained when the leucine was dissolved in solutions of sodium hydroxide and the influence of the relative proportions in which the two substances are present on the value of the specific rotation:

Molecules of sodium hydroxide/ molecules of leucine.	$[\alpha]_D$	Molecules of sodium hydroxide/ molecules of leucine.	$[\alpha]_D$
0.54	-0.58°	1.75	5.39°
0.59	+0.88	1.97	4.37
0.83	3.09	2.30	4.60
0.86	4.42	2.54	6.74
0.99	4.00	2.58	4.90
1.30	7.51	3.75	4.93
1.63	4.98		

These figures do not show quite the same regularity as those arrived at from the acid solutions, but it is quite evident that the effect of the alkali on the specific rotation of the leucine is of a similar nature to the influence of the hydrogen chloride. A small increase in the quantity of alkali has a considerable effect on the optical activity when the molecular ratio of alkali to leucine is less than one, but produces little change in other cases. The devia-

FIG. 1.



tions shown in a few cases are probably due to errors in the reading of the rotation owing to the solution not being quite clear. It is, of course, possible that some of the irregularity might be explained by the substance undergoing partial racemisation in alkaline solution, but no evidence of this has been obtained, an alkaline solution of leucine, containing an excess of sodium hydroxide, showing no appreciable variation in optical activity when kept for some hours at 25°.

*Glutamic Acid*,  $\text{HO}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ .

An aqueous solution gave the value for the specific rotation as  $[\alpha]_D^{12.62^\circ}$ .

The results obtained in hydrogen chloride solution are shown below; it will be observed that the general effect produced by the added acid is similar to that noticed with leucine:

Molecules of hydrogen chloride/ molecules of glutamic acid.	$[\alpha]_D$ .	Molecules of hydrogen chloride/ molecules of glutamic acid.	$[\alpha]_D$ .
0.54	23.04°	1.55	30.94°
0.82	26.88	2.26	31.10
0.84	28.84	4.53	32.36
1.01	27.91		

Becker (*loc. cit.*) observed that the influence of acetic acid on the specific rotation of aspartic acid was very much less than that of hydrochloric acid. It appeared probable that this was due to the very much weaker nature of acetic as compared with hydrochloric acid, and a similar effect would be expected in the case of glutamic acid. Experiments were accordingly conducted to ascertain the effect of varying amounts of acetic and of chloroacetic acid on the specific rotation of glutamic acid; the results obtained are given in the following tables:

Molecules of acetic acid/ molecules of glutamic acid.	$[\alpha]_D$ .	Molecules of chloroacetic acid/ molecules of glutamic acid.	$[\alpha]_D$ .
1.47	13.90°	0.28	16.64°
3.92	13.86	0.55	18.68
		1.24	18.73
		1.47	19.80
		4.41	24.30

The relative effect produced by the three acids is well shown in Fig. 2, and it is quite evident from the nature of the results that the magnitude of the change produced in the specific rotation of glutamic acid depends on the strength of the added acid.

Very interesting results were arrived at when the rotation of alkaline solutions of glutamic acid was determined. The figures obtained are given in the following table, whilst the influence of a variation in the proportion of alkali present is very well shown in Fig. 3; the last point is not shown on the curve.

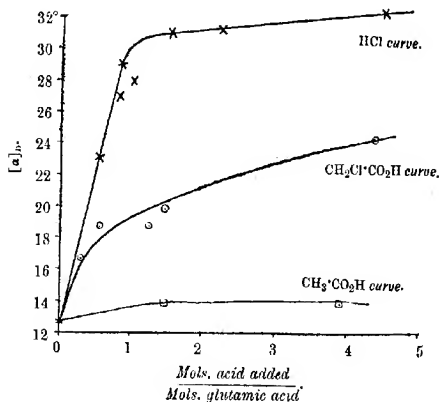
Molecules of sodium hydroxide/ molecules of glutamic acid.	$[\alpha]_D$ .	Molecules of sodium hydroxide/ molecules of glutamic acid.	$[\alpha]_D$ .
0.49	+3.00°	1.32	-0.40°
0.74	-0.40	1.60	+4.50
0.99	-4.73	2.47	10.22
1.09	-3.97	5.96	10.90

The curve shows a well-defined minimum, which corresponds with the ratio of alkali and glutamic acid necessary for the formation of the acid salt; as the proportion of alkali is still further increased the specific rotation is again rapidly changed until the molecular ratio is a little greater than two, after which no appreciable alteration in the magnitude of the specific rotation takes place on the addition of further amounts of alkali.

*Aspartic Acid*,  $\text{HO}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ .

The aqueous solution of the acid gave the value for the specific rotation as  $[\alpha]_D 5.87^\circ$ .

FIG. 2.



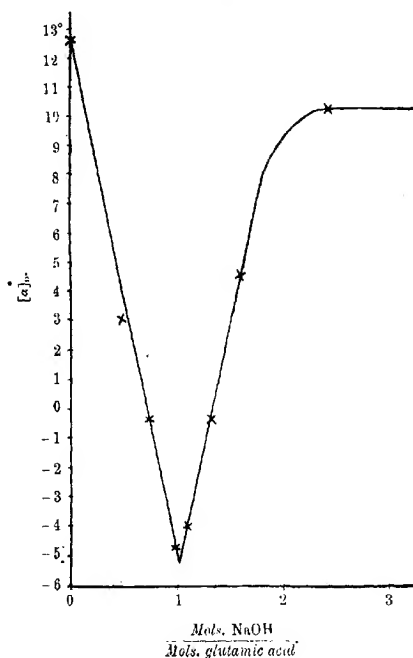
The figures obtained from solutions containing varying amounts of hydrogen chloride are shown in the following table, and the curve drawn from it shows that the influence of hydrogen chloride on the specific rotation of aspartic acid is similar in character to the effect noticed in the previous cases.

Molecules of hydrogen chloride/ molecules of aspartic acid.	$[\alpha]_D$	Molecules of hydrogen chloride/ molecules of aspartic acid.	$[\alpha]_D$
0.29	9.0°	1.44	21.6°
0.39	11.8	1.96	22.8
0.50	14.1	3.04	23.6
0.94	18.4	4.90	23.9
1.28	19.0		

The results obtained, using solutions of aspartic acid in sodium hydroxide, are shown below, and if a curve is drawn from them

It will be seen that the effect of varying proportions of alkali on the optical activity is similar to that obtained with glutamic acid. It may be mentioned that no evidence has been obtained either with aspartic acid or glutamic acid to indicate that these com-

FIG. 3



pounds undergo racemisation when in the presence of an excess of sodium hydroxide:

Molecules of sodium hydroxide/ molecules of aspartic acid.	$[\alpha]_D$	Molecules of sodium hydroxide/ molecules of aspartic acid.	$[\alpha]_D$
0.42	-3.54°	2.17	-5.1°
0.86	-14.7	2.80	-3.77
1.08	-14.5	4.96	-3.47
1.53	-9.9	6.21	-3.47



*Discussion of Results.*

It will be quite apparent from the data and curves given above that with each of the substances examined the influence of a strong acid or base on the optical activity of the compound follows the same course. In every instance the addition of the acid or base produces a marked change in the specific rotation until the molecular ratio of added substance to amino-acid is somewhat greater than one, after which the addition of further quantities of acid or base produces but little effect. In the case of the addition of sodium hydroxide to glutamic and aspartic acids it is, of course, the second portion of the curve which must be considered more particularly, the first portion of which the substance is becoming increasingly levorotatory, corresponding with the formation of the acid salt; it will be noticed that the minimum value corresponds in both cases with the ratio of alkali and amino-acid necessary for the production of the acid salt. From this point onwards the further addition of sodium hydroxide leads to variations in the specific rotation analogous to those produced by hydrogen chloride or by sodium hydroxide when added to leucine. In every case there is a distinct break in the curve, and it will be noted that this break never occurs at a point where the ratio of added acid or base to amino-acid is equal to unity, but always at a point showing a preponderance of acid or base; in other words, an excess of acid or base over the amount required to form a salt with the amino-acid must be added before this break in the curve is reached. It seems perfectly evident that this marked break in the curve is indicative of a change in the mode of existence of the amino-acid in the solution. The only change which can take place is that of the formation of a salt with the added acid or base; this change is taking place from the very commencement of the addition of the acid or base, and is indicated by the variation in the specific rotation, the value for which until salt formation is complete will be somewhere between the values for the free amino-acid and the salt. The break in the curve may therefore be taken as indicating the completion of salt-formation with the added acid or base, and the further slight changes which follow from the addition of more acid or base as being simply due to changes in the degree of ionisation. The value of the specific rotation corresponding with the break in the curve may therefore be regarded as the optical activity of the salt of the amino-acid.

When one considers the great disparity between the strength of hydrochloric acid and sodium hydroxide and the amino-acids regarded as acid and base respectively, it appears exceedingly

improbable that any appreciable excess of hydrogen chloride or sodium hydroxide would be required to decompose the internal salt supposed to exist in the aqueous solution of the amino-acid. The excess of acid or base necessary, therefore, to obtain complete salt-formation cannot be attributed in this case to the competition of two acids for a base or vice versa. This does not indicate that no internal salt exists in solution, and that no competition of two acids for a base may take place. The very different results obtained when a weak acid is used instead of hydrochloric acid are probably largely due to such competition. The true explanation of why an excess of acid or base is necessary would seem to lie in the fact that the salts of such a weak base or acid as is an amino-acid must be considerably hydrolysed in solution, so that when the amino-acid and the added substance are present in the solution in equivalent quantities some of the amino-compound must be present in the free condition. The addition of a further amount of acid or base will, of course, convert this free amino-acid into the salt and salt-formation will be practically complete provided a sufficiently large excess of hydrochloric acid or sodium hydroxide is employed. It becomes possible, therefore, to determine the degree of hydrolysis of the salts of amino-acids from the values obtained for the specific rotation in the different solutions, and knowing the degree of hydrolysis and the concentration of the solution, the basic and acidic ionisation constants of the amino-acid can be calculated. In the case of aspartic and glutamic acids, the acid ionisation-constant determined is, of course, that of the second and weaker hydrogen ion on which the hydrolysis of the salt depends.

As an example, the case of leucine hydrochloride may be taken. The specific rotation of the free amino-acid is  $-9.84^\circ$ , and that of its hydrochloride  $+11.4^\circ$ . When the two substances leucine and hydrogen chloride are present in equivalent amounts the specific rotation is seen from the curve to have a value of  $+8.0^\circ$ . Denoting the fraction of the leucine which exists in the free condition by  $x$ , we get the equation:

$$-9.84x + (1-x)11.4 = 8,$$

which gives a value of 0.16 for  $x$ .

The hydrolysis constant is then calculated by means of the equation:

$$\frac{(\text{Active mass of hydrolysed salt})^2}{(\text{Active mass of non-hydrolysed salt})} = h = \frac{K_w}{k_b}.$$

Taking the degree of hydrolysis as 16 per cent., and the concentration of the solution as 2.2 per cent., the value of the hydrolysis constant is found to be 0.0046; the ionisation constant of water at  $25^\circ$  being  $1.2 \times 10^{-14}$ , the basic ionisation constant of leucine is

accordingly  $2.3 \times 10^{-12}$ , a figure in good agreement with that obtained by Winkelblech (*Zeitsch. physikal. Chem.*, 1901, **36**, 587).

The following table gives the various values calculated by the above method, together with values previously obtained by Winkelblech (*loc. cit.*) for some of the substances:

	Wood's value.	Winkelblech's value.
Leucine .....	$k_b = 2.3 \times 10^{-12}$	$k_b = 2.7 \times 10^{-12}$
" .....	$k_a = 1.6 \times 10^{-11}$	$k_a = 3.1 \times 10^{-10}$
Glutamic acid .....	$k_b = 3.9 \times 10^{-12}$	
" .....	$k_a = 1.0 \times 10^{-11}$	
Aspartic acid .....	$k_b = 1.3 \times 10^{-11}$	$k_b = 1.3 \times 10^{-12}$
" .....	$k_a = 2.2 \times 10^{-12}$	

The close agreement between the values for  $k_b$  obtained by the author and Winkelblech for leucine and aspartic acid is at once noticeable, and suggests that the method employed by the author might be used with advantage in the case of all optically active amphoteric electrolytes of sufficient a degree of solubility; rather greater variation is shown between the values for the acid constant of leucine.

In conclusion, the author wishes to express his thanks to the Carnegie Trustees for a grant which defrayed the cost of the materials used in the investigation.

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## CLXXXV.—The Estimation of Carbon Monoxide.

By JOSEPH IVON GRAHAM and THOMAS FIELD WINMILL.

SEVERAL methods for the estimation of carbon monoxide based on the reaction  $I_2O_5 + 5CO = I_2 + 5CO_2$  have been described,\* some involving the estimation of the iodine produced, others the carbon dioxide, the latter being usually absorbed by standard barium hydroxide, the excess of which is titrated with standard oxalic acid solution. The application of these methods to routine estimations of carbon monoxide is difficult owing to the cumbersome nature of the apparatus required, and the large volume of sample necessary. We have, therefore, devised an apparatus which is essentially a modification of the well known Haldane type of gas analysis

\* For an excellent résumé of work on this object, see Weiskopf, *J. Chem. Metall. Min. Soc. S. Africa*, 1909, **9**, 258; compare also Goutal, *Ann. chim. anal.*, 1910, **15**, 1; Levy, *J. Soc. Chem. Ind.*, 1911, **30**, 1437.

apparatus, and in which iodine pentoxide is employed for the selective oxidation of carbon monoxide, so that the latter may be quickly and easily estimated volumetrically, yet, at the same time, so that an accuracy of 0.02 per cent. may be obtained, 20 c.c. of the sample being the volume required for an analysis.

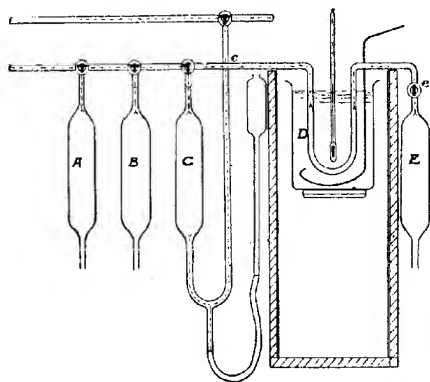
The rate of oxidation of carbon monoxide by iodine pentoxide is determined largely by the temperature at which the reaction is carried out, and this has been one of the chief points of discussion between the various investigators of this subject. We have found that the reaction takes place slowly at 70–80°, but is rapid and complete at 90–100°, and have, therefore, finally adopted the latter range of temperature. The results of a number of analyses of mixtures of carbon monoxide and air (tables A and B) show that an accuracy of 0.02 per cent. may be readily obtained.

It is well known that unsaturated hydrocarbons affect the accuracy of estimations, and these must therefore be removed from the sample before passage over the iodine pentoxide. In the present investigation considerable attention has been given to the reaction of iodine pentoxide with hydrogen and saturated hydrocarbons at various temperatures. It seems to have been generally accepted that hydrogen is not acted on by iodine pentoxide. In the following pages, however, it is shown that hydrogen in the absence of carbon monoxide is attacked by iodine pentoxide at temperatures above 135°. When carbon monoxide is present, oxidation of the hydrogen takes place at lower temperatures as the percentages of these gases increase. When the concentration of hydrogen is above 20 per cent. it is impossible to oxidise the carbon monoxide without attacking the hydrogen to some small extent, even at temperatures below 100°. The nature of the action of iodine pentoxide in the presence of carbon monoxide is not quite clear, but it seems highly probable that, with mixtures of hydrogen and carbon monoxide containing comparatively large amounts of the latter (more than 3 or 9 per cent.), the hydrogen is attacked by the nascent iodine evolved in the reaction between the carbon monoxide and iodine pentoxide. The action of iodine pentoxide on hydrogen at higher temperatures (about 160°) appears, on the other hand, to be a simple case of oxidation of the hydrogen to water with liberation of iodine. In order to estimate carbon monoxide accurately by oxidation with iodine pentoxide, if the hydrogen exceeds 20 per cent., the sample must be suitably diluted with an indifferent gas. When, however, the hydrogen is below this limit an accuracy of 0.02 per cent. in the estimation of the carbon monoxide can readily be obtained on a sample of 20 c.c. by the method described in this paper.

## EXPERIMENTAL.

*Description of Apparatus and Analytical Results for Mixtures of Carbon Monoxide and Air.*

The apparatus used is a modification of the well-known Haldane type of gas analysis apparatus, and is designed to measure the contraction which occurs when a mixture containing carbon monoxide is passed over heated iodine pentoxide and the products of the reaction are treated with potassium hydroxide. This contraction is equal in volume to the quantity of carbon monoxide present in the original sample. The usual absorption pipettes on the Haldane apparatus are replaced by three potassium hydroxide pipettes, a bromine pipette, and a U-tube containing about 2 grams of iodine pentoxide, arranged as shown in the figure.



*A* contains 25 per cent. potassium hydroxide solution. *C* and *E*, 45 per cent. potassium hydroxide solution, *B* bromine in an aqueous solution of potassium bromide, and *D* is a small U-tube so filled with powdered iodine pentoxide that the "dead space" in the tube is reduced to a minimum.

The potassium hydroxide and bromine pipettes are connected to suitable reservoirs. The pipette *C* is connected through a T-piece to the usual compensating device employed on the Haldane apparatus. After filling with pure iodine pentoxide, the U-tube is heated to 200° for three or four hours in a current of dry air, before being fitted to the apparatus. A broad wooden shield on either side protects the various pipettes from absorbing heat while the iodine pentoxide tube is being heated. The sample for analysis is taken into the burette and measured (1) with the usual precautions

adopted when using the Haldane apparatus, the U-tube of iodine pentoxide being immersed in a bath of cold water, the temperature of which is noted. The sample is then passed into the bromine pipette, *B*, where it is kept for four minutes, the burette tap and those leading to *A* and *C* being closed. By opening the necessary taps and lowering the reservoir attached to *C*, the sample is then transferred to the pipette *C*. The tap to *B* having been closed to the bromine pipette, the sample is passed several times backwards and forwards between *C* and *A* to remove all bromine vapour, and is then brought back into the burette and measured. The operation is repeated until a constant reading (2) is obtained. The difference between (1) and (2) gives the amount of carbon dioxide, hydrogen sulphide, sulphur dioxide, and unsaturated hydrocarbons. The latter are completely removed by two passages into the bromine pipette provided the amount does not exceed 5 per cent., the second passage only being necessary to "wash out" the "dead space" between the burette and the bromine pipette. The sample is next passed into the pipette *C* and the tap on this pipette opened to the U-tube, which is now heated to 90–100°, the beaker of cold water being replaced by one containing hot water and heated by means of a small Bunsen burner during the oxidation of the carbon monoxide. The sample is passed from *C* to *E* through the iodine pentoxide U-tube, *D*, twice backwards and forwards by raising or lowering the reservoir attached to *C*. By this means the carbon monoxide is oxidised to the dioxide, which, together with the iodine liberated, is absorbed by the alkali in *C* and *E*. The residual sample in the connexions between the burette, *A*, *B*, and *C*, is "washed out," and the gas sample again passed backwards and forwards twice over the hot iodine pentoxide. This has been found sufficient to remove completely all the carbon monoxide even when 15 per cent. is present in the original sample. (The complete removal of carbon monoxide has been demonstrated by constancy of volume after subjection to further passages over the hot iodine pentoxide, and also by the delicate "blood" test.) The beaker of hot water is then removed and replaced by the original beaker of cold water, and after a couple of minutes the potash level in *E* is brought to the graduation mark, the temperature of the water-bath being again noted. In cases where there is any small variation in temperature, a correction, readily determined by experiment, is applied. This correction should not exceed 0.002 c.c. per 1° change in temperature in a well-constructed iodine pentoxide tube. The sample is transferred to the burette and measured (3), the difference between (2) and (3) giving the amount of carbon monoxide present.

It will be noticed that the gas sample is confined over 45 per cent. potassium hydroxide solution during the oxidation, and is therefore not quite dry. Previous investigators have insisted that the sample must be free from moisture for complete oxidation of the carbon monoxide, but this is apparently unnecessary, although we have found it advisable to heat the iodine pentoxide to about 190° in a current of dry air after about twenty analyses. This is probably due to the fact that moisture has been present in the gas sample passed over the iodine pentoxide. For simplicity in manipulation the U-tube is connected to the apparatus by means of rubber junctions at *c* and *e*, no objection having been found to the adoption of this plan.

In the experiments described below, mixtures have been made from pure carbon monoxide, the purity of which has been controlled by combustion analysis in the Haldane apparatus.

TABLE A. *Mixtures of Carbon Monoxide and Air, Iodine Pentoxide (tube heated to 160—180°).*

Volume of carbon monoxide present in sample.	Carbon monoxide present. Per cent.	Carbon monoxide found. Per cent.	Error. Per cent.
c.c.			
0.004	0.02	0.02	± 0.00
0.015	0.08	0.10	+ 0.02
0.020	0.11	0.11	± 0.00
0.020	0.11	0.10	- 0.01
0.039	0.22	0.22	± 0.00
0.070	0.39	0.38	- 0.01
0.276	1.50	1.51	+ 0.01
0.568	3.06	3.09	+ 0.03

In the above determinations the pipette *E* contained mercury, and the gas was passed through the U-tube from the burette, the carbon dioxide produced being estimated by subsequent passage into the pipette *C*. The method described in the previous part of the paper was afterwards adopted owing to the contamination of the mercury in the burette and pipette, *E*, by the iodine liberated during oxidation.

TABLE B. *Mixtures of Carbon Monoxide and Air.*

Temperature.	Carbon monoxide present. Per cent.	Carbon monoxide found. Per cent.	Error. Per cent.
160—180°	3.43	3.41	- 0.02
160—180	10.22	10.21	- 0.01
130—140	24.13	24.14	+ 0.01
105—115	3.58	3.58	± 0.00
90—95	8.21	8.20	- 0.01
90—95	16.12	16.13	+ 0.01

*Influence of Hydrogen and Saturated Hydrocarbons on the Accuracy of the Method.*

*Mixtures of Hydrogen and Air.*—The reaction between iodine pentoxide and hydrogen at various temperatures was investigated, and from the results given below it is clear that hydrogen is readily attacked by iodine pentoxide at temperatures above 135°.

TABLE C.

Temperature.	Hydrogen in sample. Per cent.	Carbon monoxide present. Per cent.	Contraction. Per cent.
100—105°	20	0.00	0.00
110—125	100	0.00	0.00
140—145	100	0.00	0.02
160—165	100	0.00	0.35
170—180	20	0.00	0.50
170—180	100	0.00	1.27

From the above table it appears that hydrogen alone is not attacked at temperatures below 130°. When, however, carbon monoxide is present, this temperature is considerably reduced. This reduction depends both on the concentration of the hydrogen and that of the carbon monoxide. Experiment shows that: (1) If the concentration of hydrogen exceeds 20 per cent., accurate estimation of the carbon monoxide is impossible. (Table D.) (2) If the concentration of hydrogen is less than 20 per cent. but greater than 6 per cent., and that of the carbon monoxide greater than 3 per cent., accurate estimation of the carbon monoxide is still impossible. (Table E.) (3) If the mixture contains less than 20 per cent. of hydrogen and less than 8 per cent. of carbon monoxide, an accuracy of 0.02 per cent. can be obtained (Table F), and (4) If the concentration of the hydrogen is below 1 per cent., up to 25 per cent. of carbon monoxide can be satisfactorily estimated. (Table G.)

It follows, therefore, that for accurate analysis of mixtures rich in hydrogen and carbon monoxide, the sample should be diluted with air to bring the concentration of the hydrogen below 20 per cent. and that of the carbon monoxide below 8 per cent.



TABLE D. *Mixtures of Hydrogen, Carbon Monoxide, and Air, in which the Hydrogen exceeds 20 per cent.*

Temperature.	Hydrogen. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90°	23.0	5.37	5.38	+0.01
120	23.0	5.37	5.43	+0.06
105—115	27.5	11.13	11.30	+0.17
100—115	28.0	4.70	4.73	+0.03
70—80	33.0	9.86	9.81	-0.05*
100—115	35.0	4.08	4.25	+0.17
90—95	52.8	1.17	1.30	+0.13
90—95	68.2	0.72	0.79	+0.07
75—85	70.0	3.64	3.70	+0.06
100—110	80.0	2.82	3.07	+0.25
90—95	92.8	1.10	1.31	+0.21

\* Incomplete oxidation at the low temperature employed.

TABLE E. *Mixtures containing between 6 per cent. and 20 per cent. of Hydrogen and more than 8 per cent. of Carbon Monoxide.*

Temperature.	Hydrogen. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90—95	6.05	9.52	9.59	+0.07
90—95	6.05	12.41	12.57	+0.16
90—95	8.03	10.65	10.74	+0.09
90—95	18.57	9.73	9.90	+0.17
85—90	18.57	10.01	10.09	+0.08
85—90	18.72	9.57	9.70	+0.13
85—90	20.0	12.65	13.08	+0.43

TABLE F. *Mixtures containing less than 20 per cent. Hydrogen and less than 8 per cent. Carbon Monoxide.*

Temperature.	Hydrogen. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90—95	6.38	5.47	5.47	±0.00
90—95	8.30	8.44	8.44	±0.00
95—105	14.0	7.39	7.38	-0.01
95—105	14.0	7.45	7.43	-0.02
90—95	18.80	7.87	7.88	+0.01
90—95	19.58	5.66	5.68	+0.02

TABLE G. *Mixtures containing less than 3 per cent. Hydrogen with large percentages of Carbon Monoxide.*

Temperature.	Hydrogen Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90—95	2.16	11.95	12.00	+0.05
90—95	2.00	14.27	14.36	+0.09
90—95	1.20	15.96	16.00	+0.04
90—95	1.04	24.85	24.95	+0.10

The action of mixtures of air with methane, containing a small percentage of its homologues ("natural fire-damp"), has been tested with samples containing approximately 10 per cent. and 80 per cent. of combustible gas. No oxidation is observed even when the sample is passed over iodine pentoxide heated at 160–180°. Artificial mixtures of these samples with small amounts of carbon monoxide were also analysed, the results being given below:

Temperature.	Fire damp. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
160–180°	10.85	0.00	0.00	±0.00
90–95	79.0	0.00	0.00	±0.00
160–180	79.0	0.00	–0.01	–0.01
160–180	10.8	0.18	0.19	+0.01
160–180	10.7	1.12	1.15	+0.03
90–95	74.6	1.98	2.01	+0.03
90–95	70.6	2.60	2.59	–0.01

As coal gas contains a large proportion of hydrogen, it is not possible to analyse an undiluted sample for carbon monoxide.

In the following analyses the samples were consequently diluted with air to about five times their volume in order to reduce the concentration of hydrogen to about 12 per cent. for the reasons already stated. If this be done, results which do not differ by more than 0.02 per cent. may be obtained for the carbon monoxide estimation, as shown by the following table:

	Sample A.			Sample B.		Sample C.		
	(1)	(2)	(3)	(1)	(2)	(1)	(2)	
Coal gas, per cent. ....	23.17	23.17	23.17	21.04	21.04	21.98	21.98	
CO <sub>2</sub> unsaturated compounds, etc., per cent. ....	1.18	—	1.18	0.96	0.95	1.10	1.08	
CO per cent. ....	1.39	1.39	—	1.29	1.30	1.44	1.46	

The necessary dilution can be made accurately in the gas burette of the apparatus. The residual gas after removal of the carbon monoxide by the analysis was tested for traces of carbon monoxide by the delicate "blood" test with negative results.

The authors therefore conclude that carbon monoxide can be estimated rapidly and with considerable accuracy by oxidation with iodine pentoxide by the method described, provided that the precautions detailed in this paper are observed.

A practical advantage of the method is that as only a few c.c. of the sample are needed for the analyses the same small sample which suffices for the determination of other constituents, such as oxygen, methane, or carbon dioxide, is sufficient also for determining carbon monoxide.

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CLXXXVI.—*The Effect of Ring-Formation on Viscosity.*

By FERDINAND BERNARD THOLE.

IN a previous communication on the viscosity of geometrical isomerides (T., 1912, 101, 552) attention was drawn to the appreciable exaltation of viscosity that resulted when groups possessing a certain amount of residual affinity were adjacent in a molecule, thus setting up a potential ring-system. This observation suggested a fuller investigation of the effect of ring-formation on viscosity, particularly with the view of examining the effect of varying the ring-strain and of correlating the results for viscosity with those of other physical properties.

The small extent to which the influence of ring-formation on physical constants has been investigated is, no doubt, due in some degree to the comparatively recent development of systematic methods for the synthesis of *cyclo*-paraffin derivatives, for before Perkin's researches (1885 *et seq.*) only a few *cyclohexane* derivatives and the ketones *cyclopentanone* and *cycloheptanone* were definitely known. In addition to this, one must also recognise the very considerable experimental difficulty of obtaining sufficient quantities of material (except in the *cyclohexane* series) for systematic work.

The effect of ring-formation on a physical property is shown most clearly by comparing the cyclic compound with the corresponding open-chain analogue, a method which has been adopted in the present work.

This method has to some extent been used by other investigators, but in all cases (except with the hydrocarbons) the comparison has not been strictly legitimate because corresponding compounds, that is, compounds of similar chemical and structural type, have not been compared. One should not, for example, compare *cyclopropanecarboxylic acid* with *n*-butyric acid, but with *isobutyric acid*, since butyric acid contains the  $\text{CH}_2\text{CO}_2\text{H}$  group, whilst *cyclopropanecarboxylic acid* and *isobutyric acid* both contain the group  $\text{CH}\cdot\text{CO}_2\text{H}$ . Again, *cyclohexanol* (a secondary alcohol) should be compared with hexan- $\beta$ -ol or hexan- $\gamma$ -ol, and not with *n*-hexyl alcohol. A particularly curious point of view was taken by Perkin (T., 1902, 81, 292), who, in determining the effect of ring-formation on magnetic rotation, compared *cyclopropanecarboxylic acid* with formic acid.

In most cases conclusions drawn from comparisons of this type are not materially vitiated, because the properties examined were

mainly additive and only slightly constitutive. In cases where constitutive effects are appreciable, the results obtained have been irregular and of little comparative value.

For these reasons previous comparisons of open-chain and cyclic analogues are untrustworthy, but attention may be called to a few of the more prominent results that have been obtained.

*Boiling Point.*—By comparing the boiling points of corresponding closed- and open-chain hydrocarbons, alcohols, and acids, it is clear that although in every case the cyclic compound has the higher boiling point, no definite variation of the difference between *cyclo*-paraffin and paraffin derivative is noticeable.

*Refractivity.*—This property being, after molecular mass, the least constitutive of physical properties, it is only in the cases of the two- and three-membered rings that any marked abnormalities due to ring-strain are encountered. Brühl, for example, has shown (*Zeitsch. physikal. Chem.*, 1891, 7, 179) that the observed molecular refractivities of unsaturated compounds are higher by about 1.8 than the calculated values.

The same worker, and also Tschugaev and Zelinski, have shown a similar, although smaller, anomaly in the three-membered rings.

The average value of this anomaly for *cyclo*propane derivatives is smaller than for ethylenic compounds, averaging about 0.82.

In the *cyclobutane* series little evidence is available, but Brühl (*Ber.*, 1899, 32, 1222) states that *cyclobutanecarboxylic acid* shows an anomaly of 0.53. This result may be slightly too high, but it clearly falls below the average anomaly in the trimethylene derivatives.

The five- and six-membered systems possess the least internal strain according to Baeyer's theory, and accordingly very small anomalies in the molecular refractive power are found here.

Beyond the *cyclohexane* series the only compounds examined have been the hydrocarbons and the ketones.

The variation of anomaly through the complete series of ring-systems from ethylene to *cyclooctane* can be indicated to some extent by approximately averaging the values that have been obtained.

TABLE I.

Ring system.	$\Delta$ .
Ethylene .....	+1.84 average of 19 cases.
<i>cyclo</i> Propane .....	+0.82 " 6 "
<i>cyclo</i> Butane .....	+0.53 " 1 "
<i>cyclo</i> Pentane .....	+0.04 " 2 "
<i>cyclo</i> Hexane .....	+0.04 " 2 "
<i>cyclo</i> Heptane .....	-0.06 " 2 "
<i>cyclo</i> Octane .....	-0.30 " 2 "

This continuous transition is paralleled by the figures for molecular volume and viscosity.

*Molecular Volume.*—The figures quoted below (Willstätter and Bruce, *Ber.*, 1907, **40**, 3981) indicate again the striking regular variation in the difference between closed- and open-chain analogues. The results for the two- and three-membered rings are not, of course, drawn from the same series as the others, but they appear to fall into line with those drawn from the simple *cyclo*-paraffins themselves.

TABLE II.

Substance.	Mol. Vol.	$\Delta$ .	Substance.	Mol. Vol.
Hexane .....	130.4	-7.8	Hexene .....	122.6
Menthone .....	172.0	13.0	Carone.....	169.0
Butane.....	96.5	17.5	<i>cyclo</i> Butane ...	79.0
Pentane .....	112.4	21.3	<i>cyclo</i> Pentane ...	91.1
Hexane .....	127.2	22.0	<i>cyclo</i> Hexane ...	105.2
Heptane .....	142.5	24.5	<i>cyclo</i> Heptane ...	118.0
Octane .....	158.3	27.4	<i>cyclo</i> Octane ...	130.9

*Magnetic Rotatory Power.*—In magnetic rotatory power is found a property which is much more constitutive than those previously dealt with, and one might have hoped for some decisive results of ring-strain. Unfortunately no work has been done in connexion with rings beyond *cyclohexane*, and the lower ring-compounds have been compared in many cases with substances of not strictly comparable constitution. Thus *cyclopropanecarboxylic acid*, which should be compared with *isobutyric acid*, has been compared with *formic acid* and with *n-butyric acid*, the resulting anomalies for the formation of three-membered rings being widely different. The general sense of the anomaly is shown in the following table:

TABLE III.

Substance.	Mol. Vol.	$\Delta$ .	Substance.	Mol. Vol.
*Hexane .....	6.670	+0.803	Hexene .....	7.473
<i>n</i> -Butyric acid ...	4.141	-0.331	<i>cyclo</i> Propanecarboxylic acid .	4.472
<i>n</i> -Valeric acid ...	5.513	-0.465	<i>cyclo</i> Butanecarboxylic acid ...	5.048
<i>n</i> -Hexoic acid ...	6.530	-0.639	<i>cyclo</i> Pentanecarboxylic acid ...	5.891
<i>n</i> -Hexane .....	6.646	-0.982	<i>cyclo</i> Hexane .....	5.664

\* The value of  $\Delta$  for the two-membered ring varies from +0.44 to +1.24.

The general tendency noticed before for the anomaly to increase steadily through the series is apparent in this case also, although it is rather confused by illegitimate comparisons which affect this property more than those less constitutive ones previously mentioned.

In determining the effect of ring-formation on viscosity the very constitutive nature of this property has been borne in mind, and care has been taken to compare closed- and open-chain compounds

of as nearly as possible the same type, cyclic secondary alcohols, for example, being compared with open-chain secondary alcohols, and not with primary alcohols. It would, of course, have been desirable if possible to deal with a few standard types and compare the homologous members of such a series. Unfortunately this is practically impossible, and so this has only been done intermittently, as, for example, in the carboxylic acids of the three-, four-, and six-membered rings and the ketones of the five-, six-, and seven-membered rings. In some cases alternative open-chain compounds present themselves for comparison, and usually two of these have been prepared and investigated, hence affording further evidence of the effect of symmetry on viscosity.

The substances used in the investigation have with few exceptions been prepared by standard methods, but in some cases two or three methods have been tried in order to obtain the best yields. The open-chain acids were all prepared from ethyl malonate, and the ketones from ethyl acetoacetate.

*cycloPropane Series.*—The acids and esters of cyclopropane were prepared by Perkin's method from ethylene dibromide and ethyl cyanoacetate, the yields being very poor. The older method, using ethyl malonate, was first tried, but it compares very unfavourably with the cyanoacetic ester method, both as regards yield and manipulative difficulties.

Ethyl 1-acetylcyclopropane-1-carboxylate was prepared by heating ethyl sodioacetoacetate with ethylene dibromide under pressure, and fractionally hydrolysing the product.

*cycloButane Series.*—Here again ethyl cyanoacetate yields far better results than ethyl malonate on condensation with trimethylene bromide.

*cycloPentane Series.*—The only simple compounds of cyclopentane which were easily obtainable were cyclopentanone and its carboxylic ester, the starting point in each case being adipic acid. This acid is easily obtained in 80 per cent. yield by oxidising cyclohexanol with alkaline permanganate (*Ber.*, 1908, **41**, 575).

Ethyl cyclopentanonecarboxylate was prepared by Dieckmann's method of heating ethyl adipate with sodium. *cycloPentanone* can be obtained by hydrolysing this ester, but a much better yield is obtained by distilling in small portions a mixture of calcium adipate and iron filings. No advantage was found when the operation was carried out below atmospheric pressure.

In this series pyrrolidine may also be mentioned. This was prepared by internal condensation of  $\delta$ -chlorobutylamine, which was in turn prepared by von Braun's method from the phenoxy-compound. It was dried by repeated distillation over sodium.

*cycloHexane Series.*—The majority of the compounds in this series were purchased and purified by suitable means. *cycloHexane*-carboxylic acid was prepared with some difficulty by reducing benzoic acid with sodium and amyl alcohol, and removing the di- and tetra-hydro-acids produced with ice-cold neutral permanganate. The preparation is laborious, and the yield poor, but the acid obtained is pure.

The ester was prepared by heating the acid with alcohol and sulphuric acid.

Tetrahydroquinoline was prepared by reduction of quinoline with tin and hydrochloric acid and freed from unreduced quinoline by conversion into the crystalline benzoyl derivative, which was then hydrolysed with hydrochloric acid.

Of the open-chain compounds, ethylpropylamine was prepared from ethylamine and propyl bromide and butylbenzene and *o*-propyltoluene by the Fittig method. In the last two cases the yields were exceptionally poor. The hexanols were kindly lent by Dr. Pickard, and had been examined in connexion with another research.

*cycloHeptane Series.*—The only practicable starting point for syntheses in the *cycloheptane* series is the costly suberic acid, the calcium salt of which on distillation gives a 10 per cent. yield of *cycloheptanone*. It was therefore not possible to extend examination of this series beyond the ketone suberone, which was prepared as stated above and purified by means of the bisulphite compound. It was compared with dipropyl ketone and methyl amyl ketone.

It is interesting to trace the relation between ring-strain and ease of preparation of the cyclic compounds. The yield of *cyclopropane*-1:1-dicarboxylic acid from ethyl cyanoacetate is much smaller than in the case of the *cyclobutane* derivative, and whereas the yield of *cyclopentanone* from calcium adipate was about 50 per cent. of the theoretical, with *cycloheptanone* the yield was about 12 per cent.

The viscosities were determined at 25°, except in the case of *cyclohexanecarboxylic acid* and its aliphatic analogue, which were examined at 50°. The apparatus and method of observation have been described in a previous paper (T., 1913, 103, 22), but owing to the widely different viscosities to be measured (ranging from 0.003 to 0.5), a new method of calibrating the viscometer had to be used.

#### Calibration of the Viscometer.

It is well known that the Poiseuille law,  $\eta = \frac{\pi p r^4 t}{8 l v}$  or its modified form of  $\eta = \frac{\pi h g r^4}{8 l v} d.t.$ , for a liquid flowing under its own hydrostatic

pressure is only obeyed when the time of flow is comparatively large, and many investigations have been made on the variation of the time of flow produced by alterations in the driving pressure.

Grüneisen in particular, using the Ostwald type of viscometer, has made a very thorough examination of the variation of  $p \cdot t$ , as the time is reduced by increasing  $p$  and by plotting  $p \cdot t$  against  $t$  has shown that below a certain value for  $t$  the "constant"  $p \cdot t$  begins to increase at first slowly and then more and more rapidly.

In carrying out viscosity determinations most investigators use the Ostwald type of viscometer, in which a liquid flows under its own hydrostatic pressure, and calculate the viscosity from the equation  $\eta = K \cdot d \cdot t$ , the constant  $K$  of the instrument being obtained by using a liquid the absolute viscosity of which is accurately known. This method has the advantage of not requiring any compressed air reservoirs, manometers, or other complicated means of producing an artificial driving pressure, but the absence of these, of course, prevents the determination of a  $p \cdot t$ -time curve to find if the instrument is obeying Poiseuille's law under the experimental conditions of work. This can be tested, however, much more easily than by Grüneisen's method by using a series of liquids of known viscosities for calibrating the viscometer.

If the Poiseuille law holds in each case, the "viscometer constant"  $K$  will have the same value, but if  $K$  becomes smaller as the time of flow diminishes, the time of flow is evidently below the critical value necessary for the strict application of the equation  $\eta = \text{Constant} \times d \cdot t$ .

Two courses are then open. In the first place the capillary may be reduced in diameter until the time of flow for all the liquids employed is above the critical value, and  $C$  is strictly a constant. This is perhaps the most desirable method if the liquids which are to be used in the viscometer have viscosities of the same order of magnitude. In many investigations, however, liquids of very widely different viscosities must be examined, and if the most mobile liquid had a time of flow as near as possible to the "critical time," the most viscous liquid might have a transpiration time of several hours. In such a case one is compelled either to use several viscometers with capillaries of dimensions suitable to the viscosities of the liquids examined in them, or, more conveniently, to work with a single viscometer of such construction that of the substances employed all but the very mobile follow the Poiseuille law. The "constants" corresponding with times below the critical time may be found by plotting a "calibration curve" between  $K$  and time of flow, using liquids of known viscosity, and this method has been employed in the present research. The type of curve obtained

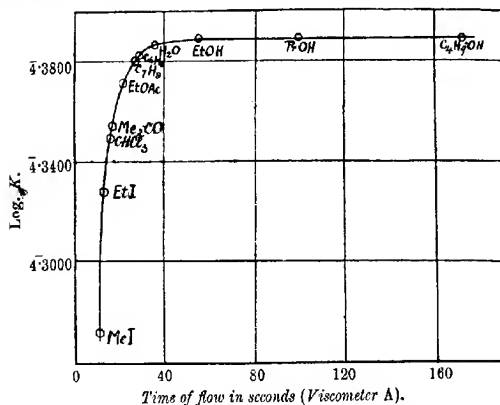


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is shown in the figure, the logarithm of  $K$  being plotted as it is the quantity employed in the calculation of viscosity.

Suitable liquids for constructing the calibration curve of a viscometer, arranged in order of increasing time of flow, are methyl iodide, ethyl iodide, chloroform, acetone, toluene, benzene, ethylene dibromide, ethyl alcohol, *n*-propyl alcohol, and *isobutyl* alcohol.

Water is not a suitable material for calibration purposes owing to its great tendency to flow irregularly over all but the most scrupulously clean glass. The viscosities of these liquids are obtained from Thorpe and Rodger's tables, and the extreme accuracy of the values is indicated by the excellent agreement of the constants obtained for times of flow above the critical time. This critical time will, of course, depend on the constructional details



of the viscometer, but with the types used by the author scarcely ever exceeds two minutes.

The actual figures for typical instruments may be quoted:

Calibrating liquid.	Viscosity <sub>sp.</sub>	Time of flow in seconds.			Log K.		
		Visco-meter A.	Visco-meter B.	Visco-meter C.	Visco-meter A.	Visco-meter B.	Visco-meter C.
Methyl iodide	0.004655	11.0	—	—	4.2720	—	—
Ethyl iodide.	0.00555	13.6	—	—	4.3280	—	—
Chloroform...	0.00535	16.2	264.2	67.6	4.3491	5.1365	5.7297
Acetone .....	0.00307	17.2	284.7	72.2	4.3542	5.1363	5.7320
Toluene .....	0.00551	26.6	—	118.5	4.3805	—	5.7324
Benzene .....	0.00602	28.5	503.0	127.4	4.3822	5.1366	5.7331
Ethyl alcohol	0.0108	56.05	—	254.3	4.3896	—	5.7329
<i>n</i> -Propyl alcohol	0.0199	101.0	—	—	4.3883	—	—
<i>iso</i> Butyl alcohol	0.0336	172.0	—	—	4.3872	—	—

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The values of  $\log K$  for viscometer *A* above the critical time are not in very good agreement, but this is an extreme case, the time of flow for this viscometer being extremely small. Viscometers *B* and *C* are the types generally used.

The numerical results are summarised below, the viscosities for the allyl and propyl compounds being drawn from Thorpe and Rodger's data.

TABLE IV.

Cyclic.		Open-chain.	
Substance.	Viscosity.	Substance.	Viscosity.
Allyl chloride.....	0.00314	<i>n</i> -Propyl chloride ....	0.00335
Allyl bromide .....	0.00472	<i>n</i> -Propyl bromide ....	0.00492
Allyl iodide .....	0.00689	<i>n</i> -Propyl iodide .....	0.00699
Allyl alcohol .....	0.0124	<i>n</i> -Propyl alcohol .....	0.0199
Ethyl cyclopropane-1:1-		Ethyl dimethyl-	
dicarboxylate .....	0.0236	malonate .....	0.0195
cycloPropanecarboxy-		isoButyric acid .....	0.0122
lic acid .....	0.0298	Ethyl isobutyrate.....	0.00557
Ethyl cyclopropane-			
carboxylate .....	0.0098	Ethyl dimethylaceto-	
Ethyl 1-acetylcyclopro-		acetate .....	0.0160
pane-1-carboxylate .....	0.0173	Menthone .....	0.0231
Carone .....	0.0339	Ethyl methylethyl-	
Ethyl cyclobutane-		malonate.....	0.0247
1:1-dicarboxylate...	0.0261	$\alpha$ -Methylbutyric acid .	0.0177
cycloButanecarboxylic			
acid .....	0.0245	Ethyl $\alpha$ -methylbutyrate	0.00675
Ethyl cyclobutanecarb-			
oxylate .....	0.00996	{ <i>n</i> -Methyl propyl ketone	0.00473
cycloPentanone .....	0.0107	{ Diethyl ketone .....	0.00442
Ethyl cyclopentanone-		Ethyl ethylaceto-	
1-carboxylate .....	0.0350	acetate .....	0.0169
Pyrolidine.....	0.00697	Diethylamine .....	0.00311
cycloHexane .....	0.00894	<i>n</i> -Hexane .....	0.00305
cycloHexanone .....	0.0280	{ Ethyl <i>n</i> -propyl ketone	0.00550
cycloHexanol .....	0.500	{ Methyl <i>n</i> -butyl ketone	0.00584
cycloHexanecarboxylic		{ Methyl <i>n</i> -butylcarbinol	0.0398
acid .....	0.0838 [50°]	$\alpha$ -Ethylvaleric acid ...	0.0206 [50°]
Ethyl cyclohexane-			0.0380 [25°]
carboxylate .....	0.0179	Ethyl $\alpha$ -ethylvalerate	0.00905
Piperidine .....	0.0137		
Tetrahydronaphthalene	0.0214	Ethyl <i>n</i> -propylamine .	0.00903
Tetrahydroquinoline .	0.0828	{ <i>n</i> -Butylbenzene .....	0.00105
cycloHeptanone .....	0.0259	{ <i>o</i> -Propyltoluene .....	0.0102
		{ <i>n</i> -Propylaniline .....	0.0253
		{ Ethyl <i>o</i> -toluidine .....	0.0200
		{ Dipropyl ketone .....	0.00685
		{ Methyl <i>n</i> -amyl ketone	0.00766

The most obvious conclusion to be drawn from the above table is that, except in the *cycloethane* series, cyclic compounds have invariably a higher viscosity than their open-chain analogues, in spite of their deficit of two hydrogen atoms. In the *cycloethane* compounds the closed- and open-chain substances have almost equal viscosities, but Thorpe and Rodger (*Phil. Trans.*, 1894, 185, 397) and Dunstan

and Thole (T., 1913, 103, 132) have shown that after making due allowance for the two hydrogen atoms the viscosity effect of the double linking is positive.

Considering the values for the separate ring-systems it is clear that in the smaller rings the difference between closed- and open-chain compound is slight, but on ascending the series the divergence increases. Ethylenic compounds, for example, have in many cases a very slightly lower viscosity than their saturated analogues; the *cyclopropane* derivatives are slightly more viscous than the corresponding propane compounds, and the divergence increases steadily to the *cyclohexane* series where the cyclic compound has a viscosity from three to five times that of the open-chain analogue. Unfortunately only one *cycloheptane* compound was available, so definite conclusions cannot safely be drawn, but in here also the viscosity exaltation is very great. Comparison of the exaltation in the ketones *cyclopentanone*, *cyclohexanone*, and *cycloheptanone* shows clearly that the value with *cycloheptanone* is only slightly less than with *cyclohexanone*, and much greater than with *cyclopentanone*.

It appears probable, in fact, that viscosity falls into line with the other physical properties in showing an anomaly which increases as the series is ascended, no reversal of this taking place as one passes the five-membered ring.

Whether this increasing anomaly in viscosity persists in still higher ring-systems can, of course, only be determined when more experimental material is available, and to this end experiments are now in progress for the synthesis of acids and esters of the higher *cyclo-paraffins*.

It is not altogether easy to suggest a reason for the high viscosity of the closed-ring compounds. It is possible that such molecules have a much more rigid structure than the open-chain compounds, and therefore one might expect a greater difficulty in flowing, a difficulty which would naturally increase with the size of the rigid structure.

Attention may be drawn to the interesting additional evidence of the effect of symmetry on viscosity, a point which the author has previously demonstrated (T., 1912, 101, 1011).

Five cases of isomeric pairs are indicated in table IV, and of each pair the more symmetrical compound is the less viscous.

The author desires to express his indebtedness to the Research Grant Committee of the Chemical Society for a grant which has covered much of the cost of the investigation.

TECHNICAL COLLEGE,  
EAST HAM.

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CLXXXVII.—*Oxidation of Papaveraldine  
Methosulphate.*

By FREDERICK ALFRED MASON and WILLIAM HENRY PERKIN, jun.

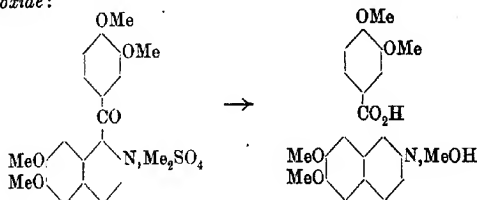
DURING the examination of the behaviour of the alkaloids towards oxidising agents, one of the chief experimental difficulties which is so frequently encountered when alkaline oxidising agents must be used is the insolubility of most of the alkaloids in aqueous liquids.

It thus happens—for example, where potassium permanganate is employed—that some of the alkaloid becomes entangled in the hydrated manganese dioxide, and escapes oxidation, whereas the part which is attacked being converted into more soluble substances, potassium salts, etc., is exposed to the further action of the oxidising agent, and yields degradation products of comparatively small molecular weight and often much oxalic acid. It is mainly for this reason that it has frequently been found so difficult to isolate the initial product of the action of the oxidising agent on the alkaloid, and that, in its place, a variety of degradation products derived from one or the other half of its molecule are the only substances which can be discovered.

This difficulty may sometimes be overcome by oxidising the alkaloid in dry acetone solution with solid permanganate, but this process is only applicable to special cases, and is sometimes quite unsuccessful.

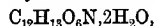
The conditions required for successful oxidation by permanganate in weak alkaline solution are obviously that a derivative of the alkaloid should be employed which is readily soluble in water, and is not decomposed by weak alkalis. While considering these conditions, it occurred to one of us that the ideal derivatives for this purpose are probably the methosulphates of the alkaloids, since these are easily prepared, and are usually soluble and not decomposed except by concentrated alkali. In order to test this possibility, experiments on the oxidation of the methosulphates of several of the leading alkaloids have been undertaken, and one of the first to be investigated has been papaveraldine (xanthaline), of which, owing to the generosity of Messrs. T. and H. Smith, we happened to have a considerable supply. We desire again to thank this firm and Dr. Dey, the managing director, for the gift of large quantities of valuable material and the interest they have taken in these researches. Papaveraldine methosulphate may be prepared readily and quantitatively by simply mixing the components; it is a crystalline substance (p. 1616), very readily soluble in water, and is not decomposed by dilute alkali. When, however,

it is heated with concentrated potassium hydroxide, it suffers fission into veratric acid and 3:4-dimethoxyisoquinoline metho. hydrozide:



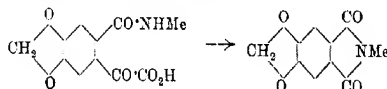
The oxidation of papaveraldine methosulphate by alkaline permanganate proceeds quite readily at the ordinary temperature, and leads to the formation of veratric acid and of three other main products, which are called *A*, *B*, and *C* in the experimental part of this paper (p. 1818).

The substance *A* is a crystalline acid of the formula



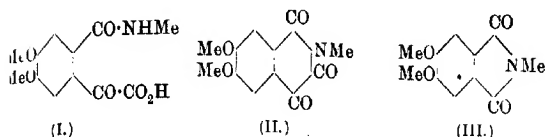
which melts at 107°, and the investigation of this acid seems to us to prove conclusively that it is 3:4-dimethoxy-6-methylcarbamyl-phenylglyoxylic acid (I). This glyoxylic acid dissolves in hydrochloric acid, and, if the solution is boiled, crystallisation soon commences and 1:3:4-triketo-6:7-dimethoxy-2-methyl-1:2:3:4-tetrahydroisoquinoline (II) separates in bright yellow needles. When the glyoxylic acid is digested with dilute nitric acid it is partly oxidised, and a crystalline substance melting at 267° is formed, which investigation has shown to be *m-hemipinmethylimide* (III), and the same change takes place when the acid is treated with other oxidising agents, such as bromine water or permanganate\*:

\* In this connexion it is of interest to notice that Freund (*Ber.*, 1899, 22, 456, 1156, 2322, 2329; *Annalen*, 1892, 271, 320) has observed that hydrastine, when oxidised with permanganate, yields hydrastinic acid and that this acid is oxidised by nitric acid to the methylimide of hydrastinic acid:

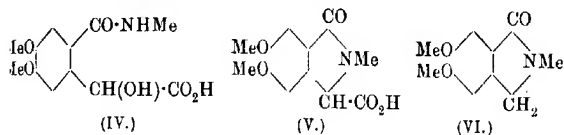


and also that Freund and Beck (*Ber.*, 1904, 37, 1942) have prepared the parent substance of II from *N*-methyltetrahydroisoquinoline by oxidation with chromic acid:

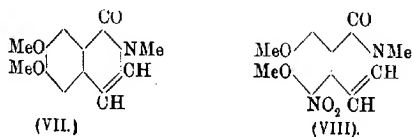




Since *m*-hemipinmethyliamide had not previously been described, we prepared it by distilling the methylamine salt of *m*-hemipinic acid (p. 2021), and find that it melts at 266–267°, and that it is identical, not only with the substance obtained from the glyoxylic acid as described above, but also with *B*, which is one of the substances formed during the oxidation of papaveraldine methosulphate with permanganate. When the glyoxylic acid is reduced by sodium amalgam or by tin and hydrochloric acid, it is doubtless in the first place converted into the corresponding glycollic acid (IV), but this undergoes internal condensation with loss of water, and yields 3:4-dimethoxyphthalimidine-1-carboxylic acid (V). This interesting acid melts at 147–150° with gradual decomposition, and when it is heated at 170–180° the change is rapid, carbon dioxide is eliminated, and 3:4-dimethoxyphthalimidine (VI) is produced, a substance which melts at 145–146°, and is oxidised by acid permanganate to *m*-hemipinmethyliamide (III):



The substance *C*, which under certain conditions (p. 2021) is produced in large quantity during the oxidation of papaveraldine methosulphate with permanganate, is a base, characterised by the insolubility of its hydrochloride in hydrochloric acid. Examination has shown that this base is 6:7-dimethoxy-2-methylisocarbostyryl (VII), a substance which had already been obtained by Pschorr and Decker and Koch (compare p. 2022), and it is further characterised by the fact that it yields a crystalline nitro-derivative, of the probable constitution (VIII), which has been prepared by Pyman (T., 1910, **97**, 270) by a different process, and melts at about 245°:



Since it is clear that 3:4-dimethoxy-6-methylcarbamyphenylglyoxylic acid must be derived from the dimethoxyisoquinoline portion of the molecule of papaveraldine, it seemed interesting to determine whether the same acid could be obtained from dimethoxyisoquinoline itself by a similar process of oxidation. In order to test this, the base (compare T., 1911, **99**, 135) was combined with methyl sulphate, and the crystalline additive product oxidised with permanganate under the conditions given in detail on p. 2023, when it was found that the product of oxidation contained considerably quantities of the glyoxylic acid.

#### EXPERIMENTAL.

##### *Papaveraldine Methosulphate.*

This substance is readily prepared by thoroughly mixing papaveraldine (50 grams) with pure methyl sulphate (50 grams) in a mortar, when a yellow paste is formed which is then transferred to a beaker and heated on the steam-bath until a clear, deep yellow syrup is produced. Methyl alcohol (80 c.c.) is then added, the solution well stirred and allowed to remain for about an hour until the whole has set to a thick, microcrystalline paste.

The methosulphate is collected, washed with a little methyl alcohol, drained on porous porcelain, and dried in the steam-bath.

For analysis, the substance was recrystallised from methyl alcohol, from which it separates as a lemon-yellow, microcrystalline powder containing approximately one molecule of methyl alcohol of crystallisation:

0.5897 \* lost 0.0308 at 100°. MeOH = 5.2.

$C_{20}H_{19}O_5N, Me_2SO_4, MeOH$  requires MeOH = 6.3 per cent.

0.2326 † gave 0.4638  $CO_2$  and 0.1070  $H_2O$ . C = 54.4; H = 5.1.

0.2013 † „ 0.1033  $BaSO_4$ . S = 7.0.

$C_{22}H_{23}O_5NS$  requires C = 55.1; H = 5.2; S = 6.6 per cent.

*Papaveraldine methosulphate* is readily soluble in water or boiling methyl or ethyl alcohols, but sparingly so in chloroform or benzene.

Potassium hydroxide, when added to the aqueous solution, produces an orange precipitate which dissolves in excess of the alkali, and when the orange solution is boiled hydrolysis takes place with the formation of veratric acid and a basic substance, which is probably dimethoxyisoquinoline methohydroxide.

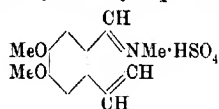
After heating for half an hour on the steam-bath, the product was filtered from a small amount of tar and mixed with excess of hydrochloric acid, when an immediate precipitate of veratric acid

\* Air-dried.

† Dried at 100°.

was obtained, and, after removing this, the filtrate was nearly neutralised and concentrated on the steam-bath. The filtrate from the inorganic salts was then allowed to evaporate to dryness over potassium hydroxide in a vacuum, when a mass of buff crystals resulted, and, after crystallising several times from 90 per cent. alcohol, the substance was obtained in lemon-yellow spherules, which, when rapidly heated, melted at 257—259°.

On examination, this substance proved to be the *hydrogen sulphate of 6:7-dimethoxy-N-methylisoquinoline*:



(compare p. 2014):

0.1664 gave 0.1246 BaSO<sub>4</sub>. SO<sub>4</sub> = 31.3.

C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>N.HSO<sub>4</sub> requires SO<sub>4</sub> = 31.9 per cent.

The *platinichloride* was prepared in the usual manner, and analysed:

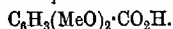
0.1675 gave 0.0396 Pt. Pt = 23.6.

(C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>N)<sub>2</sub>.H<sub>2</sub>PtCl<sub>6</sub> requires Pt = 23.8 per cent.

The identity of the substance was further confirmed by the preparation of the *picate*, which separated from boiling water in lemon-yellow needles, melted at 221—223°, and was identical with the *picate* prepared from a pure specimen of *dimethoxyisoquinoline methosulphate* (p. 2023).

#### *Oxidation of Papaveraldine Methosulphate.*

In carrying out this operation, the methosulphate (50 grams), dissolved in water (500 c.c.), was mixed with concentrated aqueous potassium hydroxide (25 grams KOH), and then a cold saturated solution of permanganate, corresponding with four atoms of oxygen (40 grams) was gradually added, the whole being cooled from time to time so that the temperature did not rise above 30°. As soon as the decolorisation of the permanganate was complete, the product was heated on the steam-bath, filtered, and the filtrate and washings of the manganese precipitate cooled and mixed with excess of hydrochloric acid, when, in a few minutes, the pale yellow liquid became pasty owing to the separation of veratric acid,

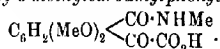


This was removed by filtration, and the filtrate allowed to remain in the ice-chest for twelve hours, during which a considerable crop of a substance (A, p. 2018) separated in glistening, colourless plates, and was collected and washed with a little water. The mother



liquor was neutralised with dilute potassium hydroxide, and concentrated considerably by distillation under diminished pressure, when, on keeping, a mass of feathery crystals separated (*B*, p. 2020). The filtrate from these crystals was then evaporated nearly to dryness, and the residue extracted twice with hot alcohol, the potassium chloride was removed by filtration, washed with alcohol, and the filtrate and washings evaporated from the steam-bath under diminished pressure, when a viscid, brown syrup remained. When this syrup was stirred with a little concentrated hydrochloric acid it became semi-solid owing to the separation of a pale buff mass of minute, felted needles (*C*, p. 2021), which were collected and drained on porous porcelain.

3:4-Dimethoxy-6-methylcarbamylphenylglyoxylic Acid,



The substance (*A*), obtained by the oxidation of papaveraldine methosulphate in the manner just described, was several times recrystallised from water and dried in a vacuum desiccator:

0.3135 gave 0.5408  $\text{CO}_2$  and 0.1610  $\text{H}_2\text{O}$ .  $\text{C}=47.1$ ;  $\text{H}=5.7$ .\*

0.6686 „ 27.2 c.c.  $\text{N}_2$  at  $16^\circ$  and 758 mm.  $\text{N}=4.7$ .

$\text{C}_{12}\text{H}_{13}\text{O}_6\text{N}_2\text{H}_2\text{O}$  requires  $\text{C}=47.5$ ;  $\text{H}=5.6$ ;  $\text{N}=4.6$  per cent.

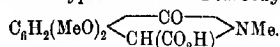
*Titration*.—0.6032, dissolved in water, required 20.8 c.c.  $\text{N}/10\text{-NaOH}$  for neutralisation, whereas this amount of a monobasic acid,  $\text{C}_{12}\text{H}_{11}\text{O}_8\text{N}$ , should neutralise 19.9 c.c. The water of crystallisation was determined by heating a weighed quantity of the substance at  $190^\circ$  by means of a glycerol bath in a small flask connected with a calcium chloride absorption tube, while a stream of dry air was passed, when 1.1590 lost 0.2050, whereas the calculated loss is 0.2065.

3:4-Dimethoxy-6-methylcarbamylphenylglyoxylic acid melts at  $107^\circ$ , with evolution of gas, to a yellow syrup; it is sparingly soluble in cold, but readily so in hot, water; it also dissolves readily in methyl and ethyl alcohols and in acetone, but is sparingly soluble in benzene and almost insoluble in light petroleum. This acid does not appear to yield an acetyl or nitroso-derivative, and it exhibits remarkable stability to the action of alkalis, since it is only slowly decomposed with evolution of methylamine when it is boiled with concentrated potassium hydroxide, and then profound decomposition takes place, so that it was not found possible to isolate dimethoxycarboxyphenylglyoxylic acid from the alkaline solution. When this solution was acidified and extracted with ether, a substance was obtained which gave an intense coloration with

\* Another analysis gave  $\text{C}=47.0$ ;  $\text{H}=5.7$ .

ferric chloride and showed similarity to nor-*m*-hemipinic acid,  $C_6H_2(OH)_2(CO_2H)_2$ .

3:4-Dimethoxyphthalimidine-1-carboxylic Acid,



The reduction of dimethoxymethylcarbamyphenylglyoxylic acid may be brought about by adding granulated tin and a drop of platinic chloride to the solution of the acid in concentrated hydrochloric acid, when, after heating for a few minutes, a mass of hair-like needles separates and melts at 147—150°. A better method of preparation is to dissolve the glyoxylic acid in dilute sodium carbonate, add excess of freshly prepared 3 per cent. sodium amalgam, and, after allowing to remain for several hours with frequent stirring, to acidify, when the new acid separates in an almost pure condition.

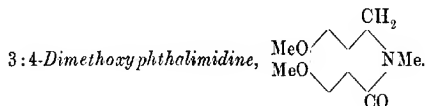
For analysis the substance was recrystallised from water and dried in the steam-bath:

0.1158 gave 0.2425  $CO_2$  and 0.0550  $H_2O$ .  $C=57.1$ ;  $H=5.3$ .

0.2070 „ 9.0 c.c.  $N_2$  at 10° and 763 mm.  $N=5.2$ .

$C_{12}H_{10}O_5N$  requires  $C=57.3$ ;  $H=5.1$ ;  $N=5.6$  per cent.

3:4-Dimethoxy-6-phthalimidine-1-carboxylic acid melts at 147—150° with gradual evolution of carbon dioxide and formation of 3:4-dimethoxyphthalimidine; it is readily soluble in hot water, and separates on cooling as a felted mass of slender needles.



When 3:4-dimethoxyphthalimidine-1-carboxylic acid is heated at 170—180° it rapidly loses carbon dioxide, and a substance is left which separates from a little water as a compact mass of felted needles:

0.1637 gave 0.3813  $CO_2$  and 0.0952  $H_2O$ .  $C=63.5$ ;  $H=6.5$ .

0.2292 „ 13.5 c.c.  $N_2$  at 17° and 745 mm.  $N=6.6$ .

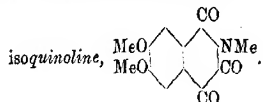
$C_{11}H_{10}O_3N$  requires  $C=63.7$ ;  $H=6.3$ ;  $N=6.7$  per cent.

3:4-Dimethoxyphthalimidine melts at 145—146°, and is sparingly soluble in cold, but readily so in hot, water; it dissolves readily in hot benzene, and separates on cooling in needles; it has basic properties, and dissolves in dilute mineral acids. This substance closely resembles *N*-methylphthalimidine, which Graebe and Pictet (*Ber.*, 1884, **17**, 1173; compare *Annalen*, 1888, **247**, 303) prepared

from potassium phthalimide by the action of methyl iodide and reduction of the methylphthalimide so obtained with tin and hydrochloric acid. This substance is readily oxidised by permanganate to methylphthalimide, and it seemed probable that a similar change would take place in the case of the dimethoxy-derivative.

In order to test this, dimethoxyphthalimidine (1 gram) was dissolved in excess of dilute sulphuric acid and oxidised by the addition of permanganate (30 c.c. of 3 per cent.), when a colourless, crystalline substance separated, which was collected, recrystallised from benzene, and recognised by its melting point (266–267°) and other properties as *m*-hemipinmethyliide (see below).

1:3:4-Triketo-6:7-dimethoxy-2-methyl-1:2:3:4-tetrahydro-



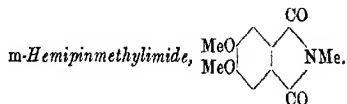
3:4-Dimethoxy-6-methylcarbamyphenylglyoxylic acid dissolves moderately readily in concentrated hydrochloric acid, and, on boiling the colourless solution, it changes to bright yellow; crystallisation soon sets in, and the mass becomes semi-solid. The precipitate was collected, recrystallised from alcohol, and dried in the steam-bath:

0.1298 gave 0.2721  $\text{CO}_2$  and 0.0532  $\text{H}_2\text{O}$ .  $\text{C}=57.4$ ;  $\text{H}=4.6$ .

0.1298 „ 9.6 c.c.  $\text{N}_2$  at 18° and 765 mm.  $\text{N}=6.0$ .

$\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}$  requires  $\text{C}=57.8$ ;  $\text{H}=4.4$ ;  $\text{N}=5.6$  per cent.

*Triketodimethoxymethyltetrahydroisoquinoline* melts and decomposes at about 270–271°, and is sparingly soluble in water or in methyl or ethyl alcohol; it dissolves in concentrated sulphuric acid, yielding an orange-brown solution. It is insoluble in cold sodium carbonate, but dissolves on boiling, yielding a colourless solution, from which, on addition of hydrochloric acid, dimethoxymethylcarbamyphenylglyoxylic acid separates.



The substance (*B*) obtained in small quantity from the product of the oxidation of papaveraldine methosulphate in the manner described on p. 2018, crystallised from acetone in needles, melting at 266–267°;

0.1399 gave 0.3085  $\text{CO}_2$  and 0.0671  $\text{H}_2\text{O}$ .  $\text{C}=60.1$ ;  $\text{H}=5.3$ .  
 0.1860 „ 10.7 c.c.  $\text{N}_2$  at  $19^\circ$  and 753 mm.  $\text{N}=6.6$ .

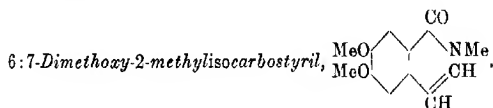
$\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$  requires  $\text{C}=59.7$ ;  $\text{H}=5.0$ ;  $\text{N}=6.3$  per cent.

This analysis and the properties of the substance seemed to indicate that it is the methylimide of *m*-hemipinic acid, and this was proved to be the case by its preparation from dimethoxymethylcarbamyphenylglyoxylic acid, and subsequently from *m*-hemipinic acid.

When dimethoxymethylcarbamyphenylglyoxylic acid is warmed with dilute nitric acid (30 per cent.), a vigorous action takes place, and the liquid soon becomes semi-solid owing to the separation of a mass of slender, felted needles. These were collected and recrystallised from benzene or acetone, when the pure substance melted at  $266\text{--}267^\circ$ , and was found to be identical with the substance (*B*) described above (Found:  $\text{C}=60.0$ ;  $\text{H}=5.2$ ;  $\text{N}=6.6$  per cent.). It was subsequently observed that the glyoxylic acid is converted into *m*-hemipinmethylimide by the action of other oxidising agents, for example, by bromine water or by potassium permanganate in the cold, and this explains its occurrence among the products of the oxidation of papaveraldine methosulphate by permanganate.

*m*-Hemipinmethylimide from *m*-Hemipinic Acid.—Since this methylimide does not appear to have been previously described, it was prepared by dissolving *m*-hemipinic acid in excess of aqueous methylamine, evaporating to dryness, and then distilling the crystalline residue, when water was eliminated and practically the whole sublimed in feathery needles.

The *m*-hemipinmethylimide thus obtained separated from benzene in small needles, melted at  $266\text{--}267^\circ$ , and was identical with the substance (*B*), which had been isolated from the product of the oxidation of papaveraldine methosulphate. It is readily soluble in chloroform, but sparingly so in alcohol, benzene, or light petroleum, and is almost insoluble in water. The solution in benzene exhibits a pale blue fluorescence.



One of the substances isolated from the product of the oxidation of papaveraldine methosulphate was a buff-coloured hydrochloride (*C*, p. 2018), and this was purified by solution in water and precipitation with hydrochloric acid, the operation being repeated until the substance was quite colourless. For analysis the substance was dried over calcium chloride in a vacuum desiccator (Found,

C=56.8; H=5.9; N=5.6; Cl=13.4.  $C_{12}H_{13}O_3N.HCl$  requires C=56.4; H=5.5; N=5.4; Cl=13.9 per cent.).

The rather high values for carbon and low values for chlorine are due to the fact that the substance slowly loses hydrogen chloride in a vacuum since the same specimen, after remaining for a week in the desiccator, contained only 13.0 per cent. of chlorine.

This hydrochloride melts at about 183–185°, and, when decomposed by alkali, yields the free base, which melts at 109°. There can therefore be no doubt that this hydrochloride is the hydrochloride of 6:7-dimethoxy-2-methylisocarbostyryl, and identical with the substance (dimethoxy-*N*-methylisoquinoline hydrochloride), which Pschorr (*Ber.*, 1904, **37**, 1932) obtained, together with 6-nitrohomoveratrole, from nitropapaverine methiodide by the action of potassium hydroxide. Pschorr states that the hydrochloride melts at 185–186°, and the free base at 107°, and Decker and Koch (*Ber.*, 1905, **38**, 1740; compare *ibid.*, 1904, **37**, 3401), who obtained the same substance from dimethoxyisoquinoline methosalts by oxidation with potassium ferricyanide, also give 185–186° as the melting point of the hydrochloride and 109–110° as the melting point of the free base. The most striking property of the hydrochloride is the fact that, although it is very readily soluble in water, it is almost completely precipitated by excess of hydrochloric acid. The picrate, prepared from the solution of the hydrochloride by the addition of picric acid, was found to melt at 137°, which agrees with the melting point observed by Pschorr for the picrate of the base prepared by his method. In connexion with the formation of dimethoxymethylisocarbostyryl from papaveraldine methosulphate, we have carried out a series of comparative experiments with the object of ascertaining the best conditions for its preparation. As the result of these we find that when papaveraldine methosulphate (50 grams), dissolved in water (1 litre), is mixed with potassium hydroxide (20 grams) and powdered ice and oxidised by the gradual addition of permanganate (35 grams) in water (1 litre) under substantially the conditions described in detail on p. 2017, that the yield of hydrochloride is at least 60 per cent. of that theoretically possible, and sometimes considerably more.

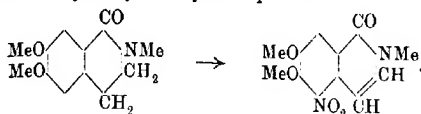
*Action of Nitric Acid.*—When the hydrochloride is warmed with dilute nitric acid (1 in 20), it dissolves, and the dark brown solution soon becomes yellow, and deposits a yellow, crystalline precipitate. This was collected and recrystallised from acetone, in which it is sparingly soluble, and was thus obtained as a felted mass of lemon-yellow needles:

0.1306 gave 0.2608  $CO_2$  and 0.0556  $H_2O$ . C=54.5; H=4.7.

0.0986 „ 9.4 c.c.  $N_2$  at 16° and 758 mm. N=10.9.

$C_{12}H_{12}O_3N_2$  requires C=54.5; H=4.5; N=10.6.

This substance is therefore the mononitro-derivative; it melts at 240—241°, and is evidently identical with 5(or 8)-nitro-1-keto-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline, which Pyman (T., 1910, **97**, 270) obtained by the action of concentrated nitric acid on ketodimethoxymethyltetrahydroisoquinoline:



and also on 6:7-dimethoxy-*N*-methylisoquinoline itself, and which softens at 240° and melts at 244—245° (corr.).

*Formation of 3:4-Dimethoxy-6-methylcarbamyphenylglyoxylic Acid from Dimethoxyisoquinoline Methosulphate.*

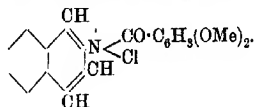
The dimethoxyisoquinoline required for these experiments was prepared from papaveraldine by fusion with potassium hydroxide according to the method described by Dobson and Perkin (T., 1911, **99**, 135).

In order to prepare the methosulphate, the base (5 grams), dissolved in benzene (30 c.c.), was gradually mixed with a solution of methyl sulphate (5 grams) in benzene (10 c.c.), when a pasty mass soon formed which was collected, drained on porous porcelain, and recrystallised from alcohol:

0.3222 gave 0.2396 BaSO<sub>4</sub>. S=10.2.

C<sub>11</sub>H<sub>11</sub>O<sub>2</sub>N.Me<sub>2</sub>SO<sub>4</sub> requires S=10.2 per cent.

*Dimethoxyisoquinoline methosulphate* separates from alcohol in colourless needles, and melts at about 202—203°. It is readily soluble in water, acetone, or methyl or ethyl alcohols, but very sparingly so in benzene. In studying the oxidation, the methosulphate (3 grams), dissolved in water (25 c.c.), was mixed with potassium hydroxide (1 gram), and, after ice had been added, a solution of potassium permanganate (4 grams) in water (50 c.c.) was slowly run in, the whole being vigorously stirred during the addition. As soon as the oxidation was complete, the product was nearly neutralised with dilute hydrochloric acid, boiled, filtered, and the filtrate and washings of the manganese precipitate evaporated under diminished pressure to about 10 c.c. The deep brown liquid was acidified with hydrochloric acid, and allowed to remain in the ice-chest, when a quantity (0.7 gram) of colourless crystals separated, which were found to consist of 3:4-dimethoxy-6-methylcarbamyphenylglyoxylic acid (p. 2018).

*Dimethoxyisoquinoline Veratroyl Chloride,*

This interesting substance is readily obtained when dimethoxyisoquinoline (2 grams), dissolved in dry ether (50 c.c.), is mixed with a solution of veratroyl chloride (2 grams) in dry ether (50 c.c.).

The precipitate which separates immediately is collected and recrystallised from alcohol, from which it separates in microscopic needles:

0.3085 gave 0.1124 AgCl. Cl=9.0.

$C_{20}H_{20}O_5NCl$  requires Cl=9.1 per cent.

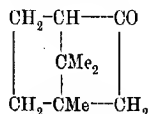
*Dimethoxyisoquinoline veratroyl chloride* melts indefinitely at about  $177-187^\circ$ , and is sparingly soluble in benzene, but readily so in chloroform, and is decomposed on warming with water. It is curious that the freshly prepared substance is bright yellow, but, on keeping exposed to the air, soon becomes colourless. This substance is isomeric with papaveraldine hydrochloride, but all attempts to convert it into this by isomeric change were unsuccessful.

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CLXXXVIII.—*d-* and *dl*-Epicamphor.

By REGINALD FURNESS and WILLIAM HENRY PERKIN, jun.

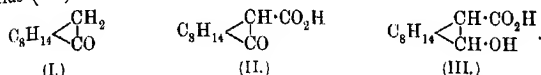
IN the previous communication (Bredt and Perkin, T., 1913, 103, 2182) it was shown that *l*-epicamphor,



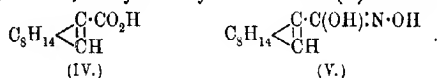
may be prepared from *d*-camphor by several different processes, and of these one of the most convenient is the following:

*d*-Camphor (I) is converted into camphorcarboxylic acid (II), and

this, on electrolytic reduction, yields the isomeric borneolcarboxylic acids (III):

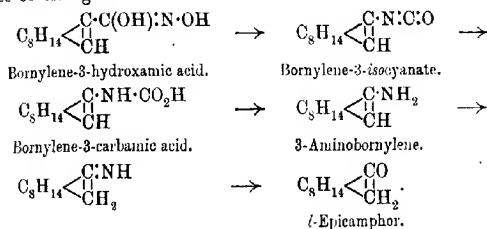


These acids readily lose water when treated with acetyl chloride with the formation of bornylene-3-carboxylic acid (IV) from the ester of which, by the action of hydroxylamine in the presence of sodium methoxide, bornylene-3-hydroxamic acid (V) is obtained:



This hydroxamic acid readily undergoes intramolecular change when it is heated or subjected to the action of toluene-*p*-sulphonyl chloride, and the product, on distillation with hydrochloric acid in a current of steam, yields *l*-epicamphor (m. p. 182°;  $\alpha_D - 58.21^\circ$ ).

This process is probably correctly represented by the following series of changes:



It will be seen that the conversion of *d*-camphor (m. p. 177–178°; +39.1°) into *l*-epicamphor ( $\alpha_D - 58.21^\circ$ ) has been accompanied by a reversal of the sign of rotation. In continuing this investigation it was thought that it would be interesting to prepare *d*-epicamphor, and this has been rendered possible by the generosity of Prof. W. J. Pope, who kindly placed at our disposal a quantity of optically pure *l*-camphor sufficient for this purpose. This was first converted, by the action of sodamide and carbon dioxide (compare T., 1913, 103, 2214), into *l*-camphorcarboxylic acid, which does not appear to have been previously described.

The acid obtained in this way crystallised well from water or from a mixture of benzene and light petroleum, melted at 125–127°, and 0.8598, dissolved in ethyl acetate and made up to 20 c.c., gave  $\alpha_D - 57.4^\circ$ .

This acid was reduced electrolytically by the process described by Bredt and his co-workers (*Annalen*, 1906, 348, 200; 1909, 366,



1) to a mixture of *l*-borneolcarboxylic acids, from which, by the action of acetyl chloride and subsequent distillation, *l*-bornylene-3-carboxylic acid was obtained. This acid, like the corresponding *d*-acid, was found somewhat difficult to purify; it was recrystallised several times from dilute acetic acid and from acetone, and then melted at 110–112°, and had, in ethyl acetate,  $\alpha_D -144^\circ$ , whereas the *d*-acid melts at 112° and has  $\alpha_D +149.5^\circ$ . The ester of this acid was next converted into *l*-bornylene-3-hydroxamic acid (m. p. 135–136°), and then into *d*-epicamphor by the process already described in detail in the case of the preparation of *l*-epicamphor (T., 1913, 103, 2206). After purification by means of the semicarbazone,\* *d*-epicamphor melted at 182°, and had, in benzene solution,  $\alpha_D +58.4^\circ$ ; the semicarbazone melted at 237–238°, and *d*-epicamphoroxime had m. p. 103° and  $\alpha_D -98.9^\circ$  in benzene solution, and these properties, except for the reversal of the sign, are practically identical with those of *l*-epicamphor.

*dl*-Epicamphor was prepared by mixing the methyl-alcoholic solutions of equal quantities of *d*- and *l*-epicamphor and precipitating by the addition of water, but larger quantities were made from *dl*-bornylene-3-carboxylic acid. This acid was obtained by mixing *d*-bornylene-3-carboxylic acid with an equal amount of the corresponding *l*-acid, and crystallising the product from dilute acetic acid; it melted at the same temperature as the active modifications, namely, at 110–112°, and was converted into *dl*-epicamphor through the hydroxamic acid in the usual manner. *dl*-Epicamphor separates from light petroleum (b. p. 50–60°, in which it is very readily soluble), especially when the highly concentrated solution is left for some days in the ice-chest, as a paste of definite crystals, and melts at 180° (uncorr.), that is to say, at practically the same temperature as the corresponding active modifications.

The *oxime* separated from dilute alcohol in needles, and melted at 98–100°, and *bromo-dl*-epicamphor, prepared by the direct action of bromine (compare *loc. cit.*, p. 2209), after recrystallisation from light petroleum, from which it separated in nodular masses, melted at 135°.

In all these cases the melting points practically coincide with those of the active epicamphors and their derivatives, and in this

\* In preparing epicamphor from the hydroxamic acid, instead of proceeding with the purification as described in the previous communication (*loc. cit.*, p. 2207), a much more advantageous method is to convert the crude epicamphor, after distillation in steam, into the semicarbazone by boiling with an equal weight of semicarbazide hydrochloride and of sodium acetate in 70 per cent. alcoholic solution for two hours.

After remaining overnight in the ice-chest, the crystalline mass is collected and washed with ice-cold alcohol until colourless; it is then mixed with hydrochloric acid and distilled in a current of steam, when pure epicamphor passes over.

respect epicamphor behaves like camphor, since the active and inactive modifications of camphor all melt at practically the same temperature, namely, at about  $178^{\circ}$ . Few only of the derivatives of *dl*-camphor have been described, but the oxime melts at the same temperature ( $118^{\circ}$ ) as the active camphoroximes, and other derivatives will doubtless be found to behave in a similar manner.

We wish to express our thanks to Messrs. R. R. Baxter and R. G. Fargher for undertaking the preparation of considerable quantities of the active epicamphors required for this investigation. We also wish to state that part of the expense of this investigation was covered by a grant from the Research Fund of the Royal Society.

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OXFORD.

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### CLXXXIX.—*The Firing of Gases by Adiabatic Compression. Part I. Photographic Analysis of the Flame.*

By HAROLD BAILY DIXON, LAWRENCE BRADSHAW, and  
COLIN CAMPBELL.

The firing of an explosive mixture of gases by rapid compression in a cylinder, according to the suggestion of Professor Nernst, appeared to offer a convenient method of determining the ignition-points of gases—provided that it could be shown (i) that the ignition is not produced locally by waves whilst the mass of the gas is still far below its ignition point, and (ii) that the piston does not move forward appreciably after the gas is raised to the ignition point. Falk's determinations, made by Nernst's method, showed, in some cases, close agreement with the results obtained by Dixon and Coward, but in others there were wide differences; for example, Dixon and Coward found the ignition-point of electrolytic gas gradually diminishes with increase of pressure, the curve indicating that at high pressures the ignition-point would lie somewhat below  $560^{\circ}$ . Falk found by adiabatic compression the ignition-point of electrolytic gas to be  $540^{\circ}$ , assuming the ratio of the mean specific heats to be 1.40. On the other hand, whilst Dixon and Coward found the ignition-point of hydrogen to be only one or two degrees higher in air than in oxygen, Falk found the ignition-point of hydrogen and air to be more than a hundred degrees higher than

the ignition-point of electrolytic gas. When, as in Falk's experiments, the piston is stopped by the explosion itself, it is obvious that if the rapidity of inflammation varies appreciably in different mixtures the true ignition-points will not be indicated by the travel of the piston. In pure electrolytic gas the rapidity of inflammation might be such as to check the piston in an inappreciably small interval of time after the ignition-point is reached, but in the mixture of hydrogen and air the slower inflammation might allow the piston to move forward appreciably during the initiation and spread of the flame. Falk, himself, states that the gases detonate practically instantaneously when the ignition-point is reached—partly on theoretical grounds, and partly because he observed no difference in the ignition-point of electrolytic gas when the weight was dropped on the piston from a greater or a less height. He

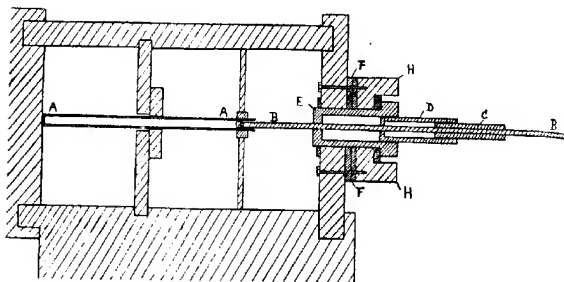


Diagram 1, showing details of arrangements for guiding and stopping piston in the compression of gases.

did not, apparently, try this experiment with one of the more slowly inflaming mixtures, such as hydrogen, with an excess of oxygen or with air.

In order to study the initiation of the flame produced by the adiabatic compression of gases, experiments were made in glass tubes so arranged that the flame could be analysed by being photographed on a rapidly moving film.

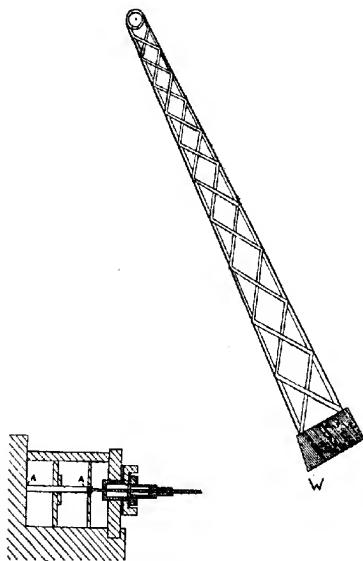
In diagram 1 AA was a stout glass tube 12 mm. in diameter and 650 mm. long containing the gases to be compressed. This tube was held by means of wooden clamps in a horizontal position with its closed end (cushioned by a pad of velvet) against a stout wooden support. The steel piston-rod BB could be rapidly forced into the tube by the falling pendulum (W), which was suspended from a beam in the ceiling by a trellis-work 3 metres long (diagram 2).

To prevent the piston-rod from buckling under the sudden

strain, it was held by three steel cases (*C, D, E*), which slid one inside the other as in a telescope, and supported the long piston as it was being pushed home.

The pendulum could be arrested at any desired point by means of the wooden blocks (*HH*), the position of which could be adjusted by inserting or removing steel plates (*FF'*)—thus allowing a smaller or greater compression.

The image of the flame was focussed by means of a lens on to the photographic film, which was fastened on to a wheel, 1 metre



*Diagram 2, showing glass tube with piston arranged for compression by falling pendulum.*

in circumference, capable of being rotated in a vertical plane at any speed between 20 and 60 revolutions per second as desired. The actual motion recorded on the film is therefore compounded of two velocities: (1) The vertical downward velocity of the film, and (2) the horizontal velocity of the image of the flame.

In the first instance experiments were made with mixtures of carbon disulphide and oxygen. Carbon disulphide was chosen because of its low ignition-point and of the actinic character of its flame.

The general appearance of the photographs obtained by the compression of mixtures of carbon disulphide and oxygen is shown on Plate 1. The films (from which the prints are directly made) were moving vertically downwards, at the rate of 20 metres per second, the tube was fixed horizontally, and the piston driven in from left to right of the photographs. Narrow strips of black paper were fastened on the tube at intervals of 25 mm. from the closed end; these form vertical dark lines on the prints at intervals of 6 mm., and serve as reference marks. The horizontal movement of the flame along the tube is thus reduced in the photograph to about one-fourth of its true amount, whilst the vertical movement is that of the film. The flame is seen to start from a point or layer, somewhat ill-defined—sometimes near the closed end of the tube as in No. 1, sometimes near the piston as in No. 2, and more often between the two as in No. 3 and 4. In No. 4 a longer column of gas was compressed. The narrow, bright streak of light seen in some of the photographs to follow the piston as it is driven back is due to the burning of the lanoline used as lubricant on the piston-head.

The flame always took an appreciable time to spread through the space occupied by the gas, and in no instance did the flame travel through the tube with a velocity approaching that of detonation. In the fastest instance observed, the flame travelled 25 mm. in  $1/4000$  of a second, that is, at 100 metres per second; whereas the explosion-wave travels in this mixture at a rate of nearly 1800 metres per second (Dixon and Russell, T., 1899, 75, 605).

In order to examine the effect of gradually increasing the compression, a series of experiments was made under as nearly as possible the same conditions, except that the piston was driven in a little further in each successive trial. The length of the column of uncompressed gas was 630 mm. in each case; in three experiments the column was compressed to 67 mm., 44 mm., and 32 mm. respectively. The photographs of the three flames taken on films moving vertically downwards at a rate of 20 metres per sec. are shown in Nos. 5, 6, and 7. In No. 7 the tube was fractured, but not before the flame had traversed the column of compressed gas. It was evident from these experiments that the piston was not stopped at the moment the gases reached their ignition-point, but at the moment the moving force was removed. The position of the collar showed that the momentum of the piston alone was not sufficient to move it appreciably after the arrest of the pendulum. Further experiments also made it clear that the piston could be driven in much further than in No. 7. *The minimum volume*



No. 1.

No. 2.

No. 3.

No. 4.

[To face p. 2030.]



No. 5.



No. 6.



No. 7.



No. 8.



No. 9.





No. 10.



No. 11.



No. 12.



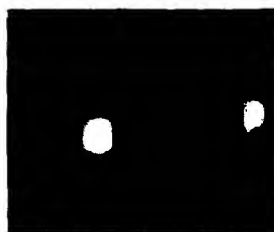
No. 13.



No. 14.



No. 15.



No. 16.

No. 17.



*observed when a gaseous mixture is fired by adiabatic compression is therefore no criterion of its ignition-point.*

Again, although it is not possible to determine in the photographs the exact moment of time when the flame reached the piston, this moment may be determined within fairly narrow limits; for instance, in No. 4 it is clear that the film had travelled downwards between 24 mm. and 30 mm. after the first appearance of the flame, and before the flame reached the advancing piston. From the known velocity of the film the flame, therefore, must have been travelling from 1.2 to 1.5 thousandths of a second before it reached the piston. During this period, however, the piston was advancing, and from its known rate must have moved 3 to 5 mm. The gas did not fire then, when the column was compressed to 76 mm. as the photograph appears to show, but when the column was still about 80 mm. long.

In order to examine what difference, if any, was made in the initiation of the flame by the rapidity with which the piston was driven in, experiments were made with all the other conditions—tube, mixture, total compression—the same, except the height from which the pendulum fell.

In Nos. 8 and 9 the gaseous column was 630 mm. long before compression, and it was compressed to 60 mm. in each case, as indicated by a collar sliding on the piston rod. The speed of the film was 20 metres per sec. in each case.

In No. 9 with a slow motion of the piston the flame is seen to travel from the firing-point at a rate not exceeding 14 metres per sec.; in No. 8 with a faster motion of the piston the flame is seen to travel with a velocity of over 60 metres per sec.

In the experiments so far made we could detect little evidence of any violent compression-waves set up by the movement of the piston. No. 8 gives evidence of feeble waves crossing the flame, but these waves appear to be the result of the initial flame itself rather than of the movement of the piston. The waves shown in No. 8 are in marked contrast to those obtained in former experiments when the gases were fired by a spark under normal pressure. In order to study what effect strong compression-waves would have on the flame under high pressure the apparatus was arranged so that the pendulum might break the primary circuit of a coil during its fall, and so induce a spark between platinum wires inserted near the closed end of the tube. The gas could thus be fired by means of a spark at any time during the compression.

Nos. 10 and 11 show the flames produced in the mixtures  $H_2 + 3O_2$  and  $2CS_2 + 5O_2$  when a spark was passed through the gases at a

point 20 mm. from the closed end of the tube at the moment the gas column was compressed from 560 mm. to 170 mm. The flames show the characteristic inflexions produced by sound-waves starting from the sparking-place and reflected from the advancing piston and the closed end of the tube. The sound-waves starting from the sparking-place move to the right and left more quickly than the flame. The sound-wave reflected from the near end (only 20 mm. distant) returns on the flame slightly retarding its advance to the right.

The sound-wave which started to the left is reflected from the piston (150 mm. distant), and returns to meet the flame advancing to the left, and checks its advance. The broad dark line on the figure is made by a clamp holding the glass tube 100 mm. from the closed end. In the original photographs one can see a faint inclined line caused by the light of the flame being reflected from the polished face of the advancing piston, and this shows the forward movement of the piston whilst the flame was approaching it. In No. 11 the sound-waves starting from the spark were reflected from end to end of the column of gases eight times before the flame reached the piston. The photograph shows that the piston continued to advance after the flame reached it, the brighter line of light marking its path being due to the burning of the lanoline used to lubricate the piston-head.

It is clear from a comparison of the photographs that the flame set up by compression does not give rise to the well-defined waves which are so conspicuous in the spark-ignited mixtures. The "compression-flame" has not the same sharp beginning; it seems to emanate from a wider area, and its advancing edges are less clearly defined than the "spark-flame." So far, then, as the photographic evidence goes, it does not appear that sound-waves due to the motion of the piston are likely to cause "premature" ignitions when the mass of the gas is below the true ignition-point. On the contrary, the photographs show that the piston continues to compress the gas after the appearance of the flame, and in certain cases even after the flame has reached the piston, and therefore the true ignition-temperature cannot be calculated from the furthest position reached by the piston in its forward movement.

#### *The Pre-flame Period.*

The foregoing experiments have shown that all explosive mixtures of gases do not "detonate" when they are fired by adiabatic compression. In the cases examined the flame, after its appearance, takes an appreciable time to spread through the mixture, and during this time the piston may continue to advance if there is

nothing to check it but the explosion itself. The real ignition-point, however, is not necessarily synchronous with the appearance of the flame. The ignition-point is the temperature at which a mass of the gas self-heats itself by combination if left to itself until it bursts into flame. If the piston move during the actual spread of the flame, a fortiori it can move during the pre-flame period.

To gain some idea as to the length of the "pre-flame" period some experiments were made with different compressions applied to the same mixture.

A slow-firing mixture containing one volume of hydrogen and three volumes of oxygen was employed. When a column of these gases 540 mm. long was compressed into a length of 40 mm. no flame was produced; but when the same column was compressed into a length of 36 mm. before the piston was stopped, a flame appeared in the centre of the compressed gases, as shown in photograph No. 12.\* On the assumption that the ratio of the specific heats of the compressed gases is 1.4, and that there was no loss of heat during compression, the gases were heated by the compression to a temperature of  $550^{\circ}$  in the first, and of  $578^{\circ}$  in the second experiment. On these assumptions the "ignition-point" of this mixture would lie between these two temperatures.

In the next experiment the piston was not stopped until the column of gases was compressed from 540 mm. to 30 mm. The temperature of the gases, calculated from the compression alone, must have been at least  $640^{\circ}$  at the moment the flame first appeared, for the photograph No. 13 shows that the piston could not have moved more than 0.5 mm. during the spread of the flame, and, consequently, the gases must have been compressed to 30.5 mm. at least before the flame started.

In the fourth experiment the piston was not stopped until the column of gases was compressed from 540 mm. to 20 mm., and the flame (No. 14) did not appear until the piston reached this point, or was not more than 0.5 mm. from it. The temperature of the gas, *calculated from the compression alone*, must have been at least  $810^{\circ}$  at this moment. In the fifth experiment the piston was not stopped until the column was compressed to a length of 13.5 mm. If the flame started when the piston was 0.5 mm. from its stopping place, and the photograph (No. 15) shows that it could not have started before, the temperature of the gas, *calculated from the compression alone*, must have been at least  $975^{\circ}$  before the flame appeared.

It is evident, then, that the "ignition-point" of this mixture

\* In this experiment and in No. 15 the tubes broke after the flame had traversed the column of gases.

(according to the first experiment, below  $578^{\circ}$ ) is a long way below the temperature at which the flame actually appears.

Some idea also may be formed from these experiments as to the time which elapsed between the moment when the "ignition-point" was reached and the moment when the flame started. If we assume that the ignition-point was just reached in the second experiment when the temperature was about  $578^{\circ}$ , and the piston was 36 mm. from the closed end of the tube, we may also assume that the ignition-point was reached in the fifth experiment when the piston arrived at the same place in its forward movement. The photograph shows, however, that in the fifth experiment the piston had time to travel forward at least 22 mm. from this position before the flame appeared. The time required for the piston to travel this distance was at least 7 mille-seconds. The heat produced by the compression from 36 to 14 mm. would have raised the temperature of the gases from  $578^{\circ}$  to  $975^{\circ}$  (approximately), and this rise of temperature would have hastened the self-heating. A pre-flame period of 7 milleseconds is therefore a *minimum* for this mixture when brought to the "ignition-point." On the other hand, by making the pendulum break an electric circuit just when the piston was stopped 36 mm. from the end of the tube, it was possible to photograph a spark on the moving film, and so to measure the time-interval between the spark and the first appearance of the flame. This gives the pre-flame period about 13 mille-seconds when the retardation of the spark is taken into account. The pre-flame period is therefore of the order of 10 mille-seconds (or  $1/100$ th of a second) for this mixture under the conditions of the experiment.

These experiments prove that the pre-flame period is not only not negligible, but that, in these mixtures, it is much longer than the flame-spreading period. Therefore, in order to determine the ignition-point by the compression, it is necessary to stop the motion of the piston artificially at the beginning of the pre-flame period.

#### *Photographs of Rapidly-firing Mixtures.*

When electrolytic gas was fired by compression, the spread of the flame was far more rapid than with excess of oxygen; but in no case was the gas detonated instantaneously, even when the fall of the pendulum was unchecked except by the explosion itself. Nos. 16 and 17 are photographs of the flames produced when the films were moving with a velocity of 50 metres per second. Although the tubes were always smashed by the explosion, the spread of the flame from a point can be observed in all. It is evident from the photographs that the flame-spreading period is negligible, and that

the piston could move but slightly during the pre-flame period if this did not greatly exceed the flame-spreading period.

In electrolytic gas the piston appears to be stopped by the explosion very shortly after the ignition-point is reached, and therefore nearly indicates the true temperature of ignition; this is not the case with weaker mixtures.

Although the photographic analysis of the flames produced by adiabatic compression had indicated the chief precautions to be taken in determining the ignition-points of gaseous mixtures, nevertheless a long series of experiments was necessary before we obtained a machine by which trustworthy results could be secured. The chief difficulties we encountered in working with a steel cylinder and piston were (i) in overcoming the friction without using a lubricant which effected the ignition-temperature, and (ii) in preventing all leakage of the compressed gas past the piston. We found, on the one hand, that when the piston was a tight-fit there was danger of premature explosions owing to the scratching of the metal; indeed, we once obtained a concordant series of readings giving a very low ignition-point to electrolytic gas, which was fired by the friction of a slight projection on the edge of the piston-cap. We found that the projection had worn a number of grooves in the wall of the cylinder, which had to be re-bored. This led us to try various metals (instead of steel) for the piston cap—a bronze being found most suitable. The use of lanoline (which made the best lubricant) was found to affect the ignition-point if any of it came in contact with the compressed gases. It was given up for some time in favour of borax or boracic acid, until the adoption of the close-fitting bronze cap allowed the use of a little lanoline on the leather washer fixed on the piston above the cap. The bronze cap made so close a sliding-fit that no inflammation of the lanoline could occur.

Our first experiments gave the ignition-point of electrolytic gas fired adiabatically as  $536^{\circ}$ ; the addition of oxygen regularly reduced the ignition-point. This series was quoted in the Presidential Address to the Society in 1910.

A later series of experiments in a rather wider tube gave  $532^{\circ}$  as the ignition-point of electrolytic gas, the ignition-points with excess of oxygen being correspondingly lower. These figures have since been reduced by the use of the more perfect apparatus described in Part II.

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MANCHESTER.



CXC.—*The Firing of Gases by Adiabatic Compression. Part II. The Ignition-points of Mixtures Containing Electrolytic Gas.*

By HAROLD BAILY DIXON and JAMES MURRAY CROFTS.

THE experiments described in Part I (preceding paper) showed what modifications of Falk's apparatus would be desirable in order to determine the ignition-point of gases by adiabatic compression. The cylinder must be sufficiently wide to prevent appreciable cooling by the walls of the central mass of gas during compression; it must be sufficiently long to give a "final volume" that can be measured with accuracy; the piston must be driven in rapidly, it must work gas-tight without the lubricant coming into contact with the explosive mixture, and it must be stopped the moment it has compressed the gas to the true ignition-point. After many experiments an apparatus was constructed that fairly met the above requirements.

*Description of Apparatus.*

A steel cylinder 56 cm. long and 11 cm. in diameter was bored with a central cavity (*C*) (Fig. 1) 30.2 mm. in diameter to a point 45 cm. from the upper end; the cavity was continued through the cylinder in order to facilitate the boring, but this lower part was enlarged, and could be closed by a steel plate (*Pt*) kept in place by means of a powerful screw (*S*). The joint was made gas-tight by means of an annular washer (*W*) of lead, which was squeezed well into place by help of the screw. Through the side-wall a hole was pierced at the bottom of the cavity, just above the steel plate, and the hole was fitted with a steel plunger (*Pl*), by means of which the cavity could be shut off during an experiment; when open, however, connexion could be made by means of the three-way glass tap (*T*<sub>1</sub>) (Fig. 2) with the gas-holder (and manometer) or with the outside air.

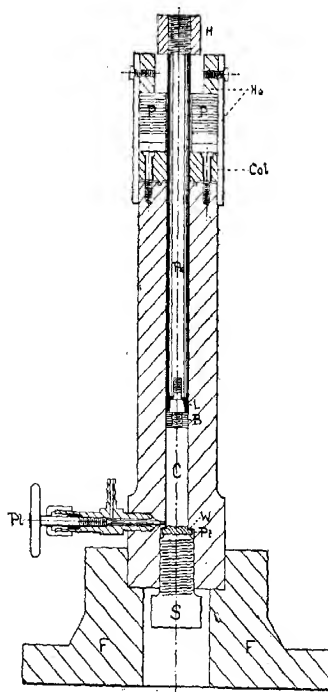
A cylindrical steel piston (*Ps*) with a head (*H*) 5 cm. long and 5 cm. in diameter fitted loosely into the explosion chamber. At its inner extremity it was furnished with a leather washer (*L*), and beyond this with a bronze cap (*B*), which made a close sliding fit with the cylinder walls.

To prevent damage to the walls it was necessary to have the piston a loose fit in the cylinder, but in its descent it was centred by means of the steel collar (*Col*), which was fastened down by means of four screws. Hard chrome-steel plates (*P*) cut with a slot could be placed on this collar, and served to stop the piston

by catching the piston-head at any desired point in its descent; these plates were made of various thicknesses—2 and 1 cm., 2, 1,  $\frac{1}{2}$ , and 0.1 mm.—and were calibrated from time to time.

The cylinder was held by an iron frame (*F*), which rested on a

FIG. 1.



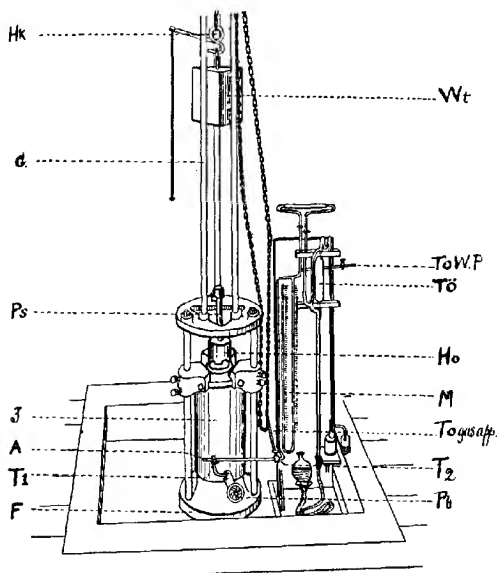
large bed of concrete; it was surrounded by a brass water-jacket (*J*), fitted with a stirring arrangement.

The compression was effected by allowing an iron weight (*Wt*) of 76 kilos. ( $2\frac{1}{2}$  cwt.) to fall from a height [usually of 1.5 metres (5 feet)] on to the piston-head—the weight falling within three iron guides (*G*).

*Method of Experimenting.*

The cylinder having been thoroughly cleaned inside, the piston was also cleaned, the leather washer lubricated slightly with lamp-oil, and pushed inside the cylinder, and its head supported by means of a stick, so that a cavity about 380 mm. long was left. The plunger (*Pl*) was opened, and the glass taps turned so as to connect the cavity with the water-pump (*WP*); a complete vacuum was obtained by finishing the exhaustion by means of the Töpler pump (*Tö*), the vacuum being measured by a mercury manometer

FIG. 2.



(*M*). The three-way tap (*T<sub>2</sub>*) was then turned so as to shut off the pumps and connect the explosion chamber with the gas-holders and drying apparatus, and the gases were allowed slowly to pass in and fill the chamber. The stick supporting the piston was then removed, and the piston pushed down until a gas chamber 377 mm. long was left. This length was measured before each experiment, and as the volumes of gas were proportional to the length of the cavity, this was taken as the initial volume in all the experiments and denoted by  $V_1$ .

Plates amounting together in thickness to the required length for  $V_2$  were put on the collar, the pressure of the manometer read, and the steel plunger screwed in tightly. Over the piston was placed a hood (*Ho*), which rested on the plates and served to take the falling weight off the piston at the moment the piston-head struck the plates.

It was always the case that when the piston was pushed right down to the bottom of the empty cylinder the head was not resting on the collar, but projected a few mm. above it; this distance was carefully measured before each experiment, and the height of the piston adjusted until a net value of 377 mm. was given for the length of the column of gases.

The weight suspended on a hook (*Hk*) was raised by means of pulleys to the required height, the steel rods which supported the weight between the experiments were withdrawn, and the weight released by pulling a string which depressed the point of the hook. An explosion, unless the explosive mixture was very much diluted, was shown by the weight being thrown back, the distances varying with the nature of the gaseous mixture.

#### *Main Sources of Error.*

(1) *Leakage.*—In all cases the piston was pulled up after the experiment until on opening the valve at the bottom the manometer showed that the original pressure had been restored—this, of course, does not apply to the pure electrolytic-gas mixture, where no gases were left after an explosion. The height of the piston was then measured, and this measurement indicated whether or no a leak had occurred in the apparatus; if a leak was found, the experiment was discarded, and the cause of the leak—usually the defective fitting of the leather washer—was investigated. When the machine was working well, the alteration in height of the manometer, when the piston was pulled up to its original height, after a non-explosion, was practically nil; and even after the weight had been dropped on the same sample of gas three or four times did not amount to more than 1 mm.

The leather washers took some little time to get into good working order, and their effective life was short.

(2) *The Lubricant.*—It was necessary to discover if the lanoline had any effect on the ignition; it was found that the same ignition-point was obtained for electrolytic gas provided that the amount of lubricant—whether lanoline, vaseline, or borax—was small, and that none was on the cylinder walls exposed to the gas during the compression. Falk (*J. Amer. Chem. Soc.*, 1906, 28, 1517; 1907, 29, 1536) used lanoline in such quantity that the piston on being

pushed into the cylinder and released, came back to its original position. We found that when the bronze-cap itself was smeared with lanoline the ignition-point of electrolytic gas was raised, some of the lanoline itself burning as well as some of the hydrogen, carbon monoxide being formed in the cylinder. We found on trial, that lanoline itself, smeared on the walls of the cylinder, was exploded when oxygen was compressed by the piston—showing that it was appreciably volatile under the conditions of our experiments. Its presence raises the ignition-point of electrolytic gas, but lowers that of mixtures requiring much higher compressions for firing. We therefore kept the bronze-cap (which fitted the cylinder closely) free from lanoline, and used the latter, in small quantity only, on the leather-washer above the cap. Under these conditions no carbon monoxide or carbon dioxide was found after the experiment if no explosion took place; and if an explosion did take place the amount of oxides of carbon formed was very small. This oxidation was an after-effect of the explosion—due to the highly-heated products of the explosion penetrating between the bronze-cap and walls, and was not a contributory cause of the explosion.

The gases were withdrawn after compression through the arm *A* of the three-way tap *T*, by pushing down the piston; they were collected over mercury and analysed.

(3) *Friction*.—A third important source of error is friction. After the bronze cap had been fitted to the piston it was seldom that friction within the cylinder interfered with the proper course of the experiments, and premature explosions were practically eliminated. More difficult to remedy was the friction of the piston against the collar, which entered it at the top of the cylinder. It was difficult to ensure that the weight on striking the piston-head did not give it an oblique thrust against one side of the collar. When this occurred the rate of fall of the piston was diminished, more cooling had time to take place in the cylinder, and consequently higher ignition-points were obtained. This error was usually detected by the same mixture yielding discordant results—which had to be discarded. The introduction of a sleeve of hard phosphor-bronze into the collar lessened the friction, although the sleeve soon worked loose and had to be renewed frequently. Only when the machine gave concordant results with electrolytic gas (agreeing with those previously obtained) were experiments made with any new gas mixture.

Traces of the rate of fall of the piston, taken on a revolving drum, and measured by means of the vibrations of a tuning-fork, showed that in the case of electrolytic gas the time occupied was about  $3/50$ ths of a second, and that the velocity of compression

was nearly constant until the piston had practically reached its lowest point.

#### *Preparation of Gases.*

The electrolytic gas was prepared by electrolysis of a saturated solution of recrystallised barium hydroxide. Oxygen was obtained by heating crystals of potassium permanganate, nitrogen by heating a mixture of ammonium sulphate, and sodium nitrite with some potassium chromate, the gas being passed through a solution of potassium dichromate in sulphuric acid. The hydrogen was prepared from pure zinc and hydrochloric acid, and washed with water. These gases were stored in large gas-holders over air-free water, which, in the case of mixtures, was previously saturated with the mixed gases; the gases were not allowed to remain for any length of time before use. In some cases mixtures of glycerol and water were used for storing.

The mixed gases before being used were analysed by means of a Bone and Wheeler gas-analysis-apparatus, and additions made, if necessary, until the desired composition was obtained.

Unless otherwise stated, the gases before entering the explosion cylinder were dried by passing through a glass worm and a drying-bottle each containing concentrated sulphuric acid.

#### *Method of Calculation.*

When a gas is compressed adiabatically, the work done on the gas produces heat, and a rise of temperature results; the amount of the rise of temperature depends on the change in volume produced and on the ratio of the specific heat of the gas at constant pressure to the specific heat at constant volume. If this ratio be denoted by  $\gamma$ , we have:

$$\frac{T_2}{T_1} = \left[ \frac{V_1}{V_2} \right]^{\gamma-1}.$$

$T_1$  and  $T_2$  represent the initial and final temperatures respectively, both being measured on the absolute scale, and  $V_1$  and  $V_2$  the initial and final volumes.

In the calculations which follow it is assumed that there is no loss of heat during the compression of the gases in the cylinder. This, of course, is not quite the case, as the compression is not instantaneous, but lasts, as already mentioned, about 3/50ths of a second in the case of electrolytic gas. The loss of heat, which must be small during this time, is difficult to estimate; it would result, of course, in the calculated temperatures being higher than those actually reached by the mass of gases in the cylinder.

In the experiments it was usual to keep  $V_1$  fixed, the volume

corresponding with a height of 377 mm., and to vary  $V_2$  in accordance with the temperature it was desired to attain in the cylinder. Some experiments were performed with  $V_2$  fixed and  $V_1$  variable, and as was to be expected, no difference was found in the results. It should be noted that in the case of electrolytic gas an error in measuring  $V_1$  of 1 mm. made a difference of  $1^\circ$  in calculating  $T_2$ , whilst an error of only 0.1 mm. in measuring  $V_2$  resulted in the same difference in  $T_2$ .

The value of  $\gamma$  for the diatomic gases hydrogen, oxygen, and nitrogen used in the experiments was taken as 1.4. Although many researches on the value of  $\gamma$  and of the specific heats of gases have been made at temperatures not exceeding the boiling point of water, comparatively few have been conducted at temperatures corresponding with those reached in the present series of experiments, and very few under the conditions of pressure which accompany the alterations in temperature.

In recent years, by the explosion method, Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536; 1910, **16**, 897) has investigated the specific heat at constant volume of hydrogen, nitrogen, and oxygen, as well as that of other gases. The formulæ which he has deduced for the mean molecular heat at very high temperatures,  $C_v = 4.7 + 0.00045$  for hydrogen and  $C_v = 4.9 + 0.00045$  for oxygen and for nitrogen, give for  $t_2 = 520^\circ$ , which is about the ignition-point of electrolytic gas,  $C_v = 4.934$  for hydrogen and 5.134 for oxygen and nitrogen. For the mixture  $2H_2 + O_2$  we have, therefore, a mean molecular heat  $C_v = 5.001$ ; and if we take  $C_p$  derived from this as 7.001, the value given for  $\gamma = 1.4$  very nearly.

There is no doubt from the experiments of all observers (for example, Holborn and Austin, *Abh. Physik. Tech. Reichsanstalt*, **4**, 131; Holborn and Henning, *Ann. Physik*, 1905, [iv], **18**, 739; 1907, [iv], **23**, 809; Langen, *Mitteilungen über Forschungsarbeiten*, **8**; Swann, *Phil. Trans.*, 1910, *A*, **210**, 199, 238; Moody, *Physikal. Zeitsch.*, 1912, **13**, 383, to mention only a few) that an increase in temperature results in an increase in the specific heat and a consequent diminution in the value of  $\gamma$ . The effect of pressure is not so clear. Joly (*Proc. Roy. Soc.*, 1894, **55**, 390, 392; 1890, **48**, 441) finds that the specific heat at constant volume increases with the pressure, except in the case of hydrogen, where a slight fall in the value was found. Valentiner (*Sitzungsber. K. Akad. München*, 1903, 691) finds the value of  $\gamma$  for nitrogen at low temperature to increase with the pressure, and hence presumably the specific heat must decrease. Holborn and Jakob (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 213) find an increase in the specific heat of air with rise of pressure.

It would therefore appear that the alteration, probably an increase in value of the specific heats with rise of pressure, is but small. It is not, however, merely the effects of increase of temperature and increase of pressure alone with which we are dealing; we are performing work on the gaseous mixture, which is being transformed into heat. It is evident that owing to the attraction of the molecules for one another more heat will be produced than corresponds with the amount of external work performed (compare Nernst, "Theoretical Chemistry," Eng. Ed., 1911, 236); this will therefore result in producing a higher temperature in the cylinder than one would otherwise expect, or, in other words, the practical value of  $\gamma$  will be increased, and this will in some degree balance the diminished value of  $\gamma$  produced by the effect of increased temperature and increased pressure acting alone.

These considerations have led to the adoption, for the sake of convenience, of a constant value for  $\gamma$  of 1.4 and for  $C_v$  of 5.0 for the diatomic gases used in the calculations of the various ignition-temperatures. In every case, however, we have given the volumes before and after the compression, so that the temperatures may be calculated for any other value of  $\gamma$ .

In the following tables we have given the initial temperature  $t_1$ , the final volume  $V_2$ , and the result of the compression—the initial volume of gases being 377.

TABLE I.



$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_1$ .	Result.
17.0	30.5	No explosion	18.7	31.3	No
17.7	27.1	Explosion	18.7	30.4	No
18.1	28.0	Explosion	18.7	30.1	Explosion
17.9	27.3	Explosion	18.7	30.2	Explosion

$$\text{Ignition-point} = 291.7 \left[ \frac{377}{30.2} \right]^{0.4} = 526^\circ.$$

The initial pressure was that of one atmosphere; the final pressure calculated from the formula:  $\frac{P_2}{P_1} = \left[ \frac{V_1}{V_2} \right]^{1.4} = 34.2$  atmospheres.

*To Test the Effect of excess of Lanoline.*

In these experiments the leather washer was freely lubricated, and the lubricant was smeared on the inner walls of the cylinder.



TABLE II.

 $2\text{H}_2 + \text{O}_2$  with lanoline.

$t_1$	$V_2$	Result.	$t_1$	$V_2$	Result.
15.7	25.1	No	16.8	23.9	No
16.3	25.3	No	16.8	22.6	No
16.6	24.6	No	17.0	20.8	Explosion

$$\text{Ignition-point} = 290 \left[ \frac{377}{20.8} \right]^{0.4} = 651^\circ \text{ roughly.}$$

After the explosion, instead of a vacuum in the cylinder, there was a considerable quantity of gas left, which on analysis was found to consist almost wholly of carbon monoxide and hydrogen.

*To Find the Ignition-temperature when the Piston was not stopped in its Downward Course.*

In these experiments the top plate was blackened with lamp-black and  $V_2$  gradually reduced until the piston-head did not touch the plate, being pushed back by the force of the explosion before it was able to do so. There was, of course, an explosion in each case.

TABLE III.

 $2\text{H}_2 + \text{O}_2 + 8\text{H}_2$ .

$t_1$	$V_2$	Result.	$t_1$	$V_2$	Result.
13.9	12.3	Plates touched	14.1	9.3	Not touched
13.9	10.3	Plates touched	14.1	10.3	Touched
14.0	7.3	Not touched	14.1	9.8	Touched
14.0	8.3	Not touched	14.1	9.5	Touched

The temperature calculated from the lowest point reached is  $288.1 \left[ \frac{377}{9.5} \right]^{0.4} = 983^\circ$ . This result should be compared with that of table XVI, where an ignition-point of  $676^\circ$  was obtained for this same mixture when the piston was artificially stopped at the moment the ignition-point was reached.

*To Test the Effect of Change in the Initial Temperature of the Mixture.*

Steam was passed through the water-jacket until a constant temperature was obtained. At first difficulty was found in keeping the leather washer on the piston end air-tight, as lanoline could not be used at this temperature. After some trials, however, we succeeded in obtaining a washer which, having been well shaped by use, did not leak, even although no lanoline was put on it. Without lubricant its effective life was short.

TABLE IV.

 $2\text{H}_2 + \text{O}_2$  with  $t_1$  at  $100^\circ$ .

$t_1$	$V_2$	Result.	$t_1$	$V_2$	Result.
100.1	57.0	No	100.1	56.3	No
100.0	54.0	Explosion	100.1	56.1	No
100.0	56.0	Explosion			

$$\text{Ignition-point} = 373.1 \left[ \frac{377}{56.0} \right]^{0.4} = 527^\circ.$$

No alteration, therefore, is found in the final ignition-point when the initial temperature of the mixture is varied, although it may be noted that the pressure in the cylinder at the moment of ignition is only  $14\frac{1}{2}$  atmospheres instead of 35 atmospheres—the pressures usually reached at room temperatures.

*The Effect of Alteration in the Initial Pressure.*

TABLE V.

 $2\text{H}_2 + \text{O}_2$ . Initial pressure, 1 atmosphere.

$t_1$	$V_2$	Result.	$t_1$	$V_2$	Result.
19.8	30.3	Explosion	20.5	30.7	Explosion
20.2	30.9	No	20.9	30.9	No

$$\text{Ignition-point} = 293.5 \left[ \frac{377}{30.7} \right]^{0.4} = 526^\circ.$$

TABLE VI.

 $2\text{H}_2 + \text{O}_2$ . Initial pressure,  $\frac{1}{2}$  atmosphere.

$t_1$	$V_2$	Result.	$t_1$	$V_2$	Result.
21.5	30.4	No	21.9	29.2	No
21.7	28.7	Explosion	21.9	28.8	No
21.7	29.6	No			

$$\text{Ignition-point} = 294.7 \left[ \frac{377}{28.7} \right]^{0.4} = 549^\circ.$$

The final pressure in this case was 18.4 atmospheres.

TABLE VII.

 $2\text{H}_2 + \text{O}_2$ . Initial pressure,  $1\frac{1}{2}$  atmospheres.

$t_1$	$V_2$	Result.	$t_1$	$V_2$	Result.
20.6	30.4	Explosion	20.8	31.0	No
20.7	30.9	Explosion			

$$\text{Ignition-point} = 293.7 \left[ \frac{377}{30.9} \right]^{0.4} = 526^\circ.$$

TABLE VIII.

 $2\text{H}_2 + \text{O}_2$ . Initial pressure, 2 atmospheres.

$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
20.0	32.2	No	20.3	31.3	No
19.8	31.2	No	20.5	30.9	No
20.3	30.4	Explosion	20.7	30.8	Explosion

$$\text{Ignition-point} = 293.7 \left[ \frac{377}{30.8} \right]^{0.4} = 527^\circ.$$

It is seen from the above experiments that changes in the initial pressure had no effect on the calculated ignition-points except in the case of the mixture, where the initial pressure was only half an atmosphere. Dixon and Coward (T., 1909, 95, 514) found a variation occurred even with small alterations of pressure near atmospheric pressure, but it would appear from their experiments that after the pressure had attained a certain value no appreciable effect on the ignition-point would result.

*Mixtures containing Excess of Oxygen.*

TABLE IX.

 $2\text{H}_2 + 2\text{O}_2$ .

$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
13.2	33.6	No	13.9	30.6	No
13.4	32.5	No	14.0	30.2	Explosion
13.6	32.1	No	14.1	30.5	Explosion
13.6	31.5	No	14.3	30.6	Explosion
13.8	31.1	No	14.5	31.0	No

$$\text{Ignition-point} = 287.3 \left[ \frac{377}{30.6} \right]^{0.4} = 511^\circ.$$

TABLE X.

 $2\text{H}_2 + 8\text{O}_2$ .

$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
14.6	31.8	Explosion	15.7	34.8	No
14.8	37.7	No	14.5	34.9	No
15.8	36.7	No	14.6	34.0	Explosion
15.9	36.1	No	14.8	34.6	No
16.1	35.8	No	14.9	34.4	No
16.3	35.4	No	15.0	34.3	Explosion

$$\text{Ignition-point} = 288 \left[ \frac{377}{34.3} \right]^{0.4} = 478^\circ.$$

TABLE XI.



$t_1$	$V_1$	Result.	$t_1$	$V_1$	Result
12.5	34.5	No	13.2	34.1	Explosion
12.9	31.3	Explosion	13.5	34.6	Explosion
13.1	32.5	Explosion	13.8	34.9	No
13.6	33.7	Explosion	13.8	34.8	No

$$\text{Ignition-point} = 286.5 \left[ \frac{377}{34.6} \right]^{0.4} = 472^\circ.$$

TABLE XII.



$t_1$	$V_1$	Result.	$t_1$	$V_1$	Result.
13.7	31.6	No	13.3	9.0	No
12.9	23.1	No	13.0	3.0	No
13.1	17.7	No			

The temperatures reached are  $500^\circ$ ,  $600^\circ$ ,  $700^\circ$ ,  $1000^\circ$ , and  $1700^\circ$  respectively, but in no instance was there an explosion; there was, however, evidence of some combination having taken place, but never of complete combustion.

The ignition-points may be tabulated thus:

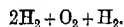
$2\text{H}_2 + \text{O}_2$	explodes at	$526^\circ$
$2\text{H}_2 + 2\text{O}_2$	"	511
$2\text{H}_2 + 8\text{O}_2$	"	478
$2\text{H}_2 + 16\text{O}_2$	"	472
$2\text{H}_2 + 32\text{O}_2$	"	—

These results are expressed in the curve (Fig. 3). The vertical line down the centre of the figure indicates the mixture  $2\text{H}_2 + \text{O}_2$ ; to the left the abscissa represents volumes of added oxygen to 3 volumes of electrolytic gas, to the right the volumes of added hydrogen or nitrogen (see later).

The limit of inflammability has evidently been passed in the last mixture.

*Mixtures containing Excess of Hydrogen.*

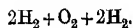
TABLE XIII.



$t_1$	$V_1$	Result.	$t_1$	$V_1$	Result.
14.0	24.0	Explosion	14.2	27.5	Explosion
14.0	26.3	Explosion	14.2	28.0	No
14.0	31.7	No	14.2	27.7	No
14.0	28.8	No	14.3	27.6	Explosion

$$\text{Ignition-point} = 287.2 \left[ \frac{377}{27.6} \right]^{0.4} = 544^\circ.$$

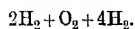
TABLE XIV.



$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
13.8	23.3	Explosion	13.5	26.7	No
13.8	23.7	Explosion	13.6	26.3	No
14.0	24.8	Explosion	13.6	26.1	Explosion
14.0	26.3	Explosion	13.6	26.2	No
13.5	27.0	No			

$$\text{Ignition-point} = 286.6 \left[ \frac{377}{26.1} \right]^{0.4} = 561^\circ.$$

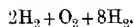
TABLE XV.



$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
14.5	24.2	No	15.0	23.2	Explosion
14.7	23.5	No	14.9	23.0	Explosion
15.0	22.9	Explosion	15.1	23.4	Explosion
15.0	23.6	No	15.0	23.5	No
15.0	23.9	No			

$$\text{Ignition-point} = 288.1 \left[ \frac{377}{23.4} \right]^{0.4} = 602^\circ.$$

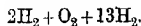
TABLE XVI.



$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
13.3	19.2	No	13.4	19.0	Explosion
13.3	18.7	Explosion	13.4	19.1	No

$$\text{Ignition-point} = 287.4 \left[ \frac{377}{19.0} \right]^{0.4} = 676^\circ.$$

TABLE XVII.



$t_1$ .	$V_2$ .	Result.	$t_1$ .	$V_2$ .	Result.
14.1	13.5	Explosion	14.4	16.3	No
14.2	14.3	Explosion	14.4	15.8	No
14.3	17.3	No	14.4	15.3	Explosion
14.3	15.3	Explosion	14.4	15.5	No

$$\text{Ignition-point} = 287.4 \left[ \frac{377}{15.3} \right]^{0.4} = 762^\circ.$$

These results may be tabulated together:

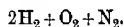
$2\text{H}_2 + \text{O}_2$	explodes at	526°
$2\text{H}_2 + \text{O}_2 + \text{H}_2$	"	544
$2\text{H}_2 + \text{O}_2 + 2\text{H}_2$	"	561
$2\text{H}_2 + \text{O}_2 + 4\text{H}_2$	"	602
$2\text{H}_2 + \text{O}_2 + 8\text{H}_2$	"	676
$2\text{H}_2 + \text{O}_2 + 13\text{H}_2$	"	762

or generally  $2\text{H}_2 + \text{O}_2 + x\text{H}_2$  explodes at  $526 + 13x$ .

These results are expressed in the curve (Fig. 3).

*Mixtures containing added Nitrogen.*

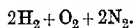
TABLE XVIII.



$t_1$ .	$V_2$	Result.	$t_1$ .	$V_2$	Result.
20.2	30.4	No	20.2	29.6	Explosion
20.2	29.4	Explosion	20.1	29.7	Explosion
20.2	29.8	No			

$$\text{Ignition-point} = 293.1 \left[ \frac{377}{29.7} \right]^{0.4} = 537^\circ.$$

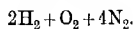
TABLE XIX.



$t_1$ .	$V_2$	Result.	$t_1$ .	$V_2$	Result.
11.2	25.6	Explosion	13.0	27.4	No
11.7	26.5	Explosion	13.3	27.0	Explosion
12.5	26.8	Explosion	13.6	27.2	No
12.7	27.6	No			

$$\text{Ignition-point} = 286.3 \left[ \frac{377}{27.0} \right]^{0.4} = 549^\circ.$$

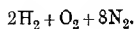
TABLE XX.



$t_1$ .	$V_2$	Result.	$t_1$ .	$V_2$	Result.
13.6	23.3	Explosion	14.2	24.8	Explosion
13.7	24.7	Explosion	14.1	25.9	No
14.0	26.3	No	14.4	25.6	No
13.9	25.5	No	15.3	25.4	Explosion
14.0	25.3	Explosion	15.4	25.7	Explosion

$$\text{Ignition-point} = 288.4 \left[ \frac{377}{25.7} \right]^{0.4} = 571^\circ.$$

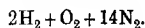
TABLE XXI.



$t_1$ .	$V_2$	Result.	$t_1$ .	$V_2$	Result.
15.4	22.5	No	14.0	22.4	Explosion
15.4	22.1	Explosion	14.5	22.6	No
15.4	22.3	Explosion	14.5	22.5	Explosion
13.3	21.3	Explosion	14.5	22.5	Explosion
13.6	22.0	Explosion	14.5	22.6	No
13.9	22.7	No			

$$\text{Ignition-point} = 287.5 \left[ \frac{377}{22.5} \right]^{0.4} = 614^\circ.$$

TABLE XXII.



$t_i$ .	$V_2$ .	Result.	$t_i$ .	$V_2$ .	Result.
15.4	21.1	No	13.0	17.7	No
15.5	20.0	No	14.0	16.7	Explosion
15.5	19.0	No	14.3	17.2	Explosion
15.5	18.1	No	14.6	17.7	No
15.5	14.1	Explosion	14.6	17.5	No
15.5	15.9	No	14.6	17.4	Explosion
12.8	14.8	Explosion	14.6	17.5	No
13.0	15.6	Explosion			

$$\text{Ignition-point} = 287.6 \left[ \frac{377}{17.4} \right]^{0.4} = 712^\circ.$$

Tabulating these results we have:

$2\text{H}_2 + \text{O}_2$	explodes at	526°
$2\text{H}_2 + \text{O}_2 + \text{N}_2$	"	537
$2\text{H}_2 + \text{O}_2 + 2\text{N}_2$	"	549
$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$	"	571
$2\text{H}_2 + \text{O}_2 + 8\text{N}_2$	"	615
$2\text{H}_2 + \text{O}_2 + 14\text{N}_2$	"	712
or generally $2\text{H}_2 + \text{O}_2 + 2\text{N}_2$ explodes at $526 + 11x$ .		

These figures are shown as a curve in Fig. 3. It will be noted that the curve is not a straight line for the whole of its length, but that the last figure found is higher than it would be if the linear function were maintained. There is no doubt that the last mixture is approaching the limit of inflammability. In the case of the hydrogen curve, with  $13\text{H}_2$ , the straight line was maintained, although such a mixture does not explode with a spark under normal conditions (see Roszkowski, *Zeitsch. physikal. Chem.*, 1891, 7, 485).

The figures obtained may be compared with those of other observers. Mallard and Le Chatelier (*Compt. rend.*, 1880, 91, 825) obtained  $550^\circ$  as the ignition-temperature of electrolytic gas, and found that addition of oxygen lowered the ignition-temperature, whilst addition of hydrogen, nitrogen, and carbon dioxide raised it. Helier (*Ann. Chim. Phys.*, 1897, [vii], 10, 521) gave  $853^\circ$  as the ignition-temperature of electrolytic gas, and stated that both oxygen and hydrogen added to the gas increase the inflammability, whilst nitrogen acts in the opposite direction.

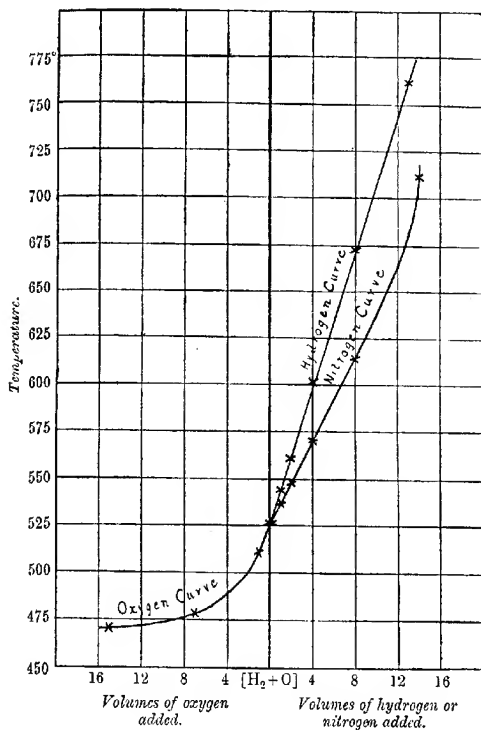
Bodenstein (*Zeitsch. physikal. Chem.*, 1899, 29, 665), following the method of Gautier and Helier, gives  $660$ — $700^\circ$  as the ignition-temperature of the mixture  $2\text{H}_2 + \text{O}_2$ , instead of  $853^\circ$ , but confirms Helier's results as to the effect of adding inert gases.

Emich (*Monatsh.*, 1900, 21, 1061) gives  $589^\circ$  as the ignition-temperature of electrolytic gas. He found that the addition of nitrogen first increases the inflammability of the gas, and then

decreases it as more nitrogen is added. Similar results were found when hydrogen or oxygen was added.

Falk (*loc. cit.*), to whose experiments reference has already been made, finds that the addition of oxygen up to that represented by the mixture  $\text{H}_2 + \text{O}_2$  lowers the ignition-temperature, but that

FIG. 3.



further addition of oxygen raises it. Addition of hydrogen and nitrogen in all quantities raises the ignition temperature.

The various temperatures found by different observers do not always refer to those of corresponding mixtures of gases, but in the table given below an attempt has been made to obtain figures which approximately indicate the ignition-temperatures for the mixtures given, so that a direct comparison can be made.



	Mallard and Le Chatelier.	Emich.	Falk.	Dixon and Crofta.
$2H_2 + O_2$ .....	550°	589°	540°	526°
$2H_2 + O_2 + 4H_2$ .....			605	602
$2H_2 + O_2 + O_2$ .....			514	511
$2H_2 + O_2 + 3O_2$ .....	531		530	(490)
$2H_2 + O_2 + 7O_2$ .....			571	478
$2H_2 + O_2 + N_2$ .....		(551)	573	537
$2H_2 + O_2 + 2N_2$ .....	(553)	(567)		549
$2H_2 + O_2 + 4N_2$ .....		(614)	649	571
$2H_2 + O_2 + 8N_2$ .....		(615)		615

The figures given in brackets have been derived from those found for mixtures of approximately the composition given by the respective observers.

Turning to the results found by our own experiments and comparing the hydrogen curve with that obtained in the case of nitrogen, it is seen that the addition of equimolecular quantities of the two gases produce a greater rise in temperature in the case of the former gas than in the case of the latter. It may be, of course, that the excess of hydrogen exercises in some unknown way a specific inhibitory effect on the reaction. We may, on the other hand, take it that we have no grounds for assuming that a higher temperature is required to explode a mixture containing an excess of hydrogen than is required for a corresponding nitrogen mixture; rather we may assume that both gases are inert in the reaction, and that the actual temperature required for explosion is the same in each case. This being granted, it follows either that the greater conductivity of hydrogen necessitates a greater compression or that the value of  $\gamma$  must be different in the two cases, and not the same as assumed in the calculations. Further experiments with argon as the diluent gas have been undertaken by one of us in order to determine the effect of dilution with a gas of known specific heat.

With oxygen added to the electrolytic gas the effect is the opposite to that found when hydrogen, nitrogen, or argon is added—the addition of oxygen results in the lowering of the ignition-temperatures. We are not in a position to offer a satisfactory explanation of this. One might imagine, as Nernst has suggested, that a peroxide is the first result of the chemical union, and therefore that the mixture containing equal volumes of hydrogen and oxygen would have the lowest temperature of ignition. Our experiments show, however, a continuous fall in the ignition-point as oxygen is added until its volume is eight times that of the hydrogen. The fall of the ignition-point with increased oxygen seems too large to be accounted for by any conceivable diminution of the specific heat of oxygen with increased concentration. Nor can the fall be due to loss of conductivity as the hydrogen is diminished, for the ignition-points rise as nitrogen is added to electrolytic gas. The

increased activity of oxygen at the higher concentrations might be explained if oxygen formed some active polymeride under these conditions, or if the concentration of the oxygen brought about ionisation of the hydrogen molecules.

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CXCI.—*The Action of Cold Concentrated Hydrochloric Acid on Starch and Maltose.*

By ARTHUR JOHN DAISH.

WILLSTÄTTER and Zechmeister (*Ber.*, 1913, **46**, 2401) have shown that whereas ordinary concentrated hydrochloric acid (37·6 per cent. HCl) acts on cellulose at the ordinary temperature relatively slowly, fuming acid (D 1·204—1·212; 39·9 to 41·4 per cent. HCl) dissolves cellulose within a few seconds and rapidly hydrolyses it, first to cellobiose and finally to dextrose. After twenty-four hours the yield of dextrose is nearly quantitative. As the present methods of estimating cellulose in plant material are of a highly empirical character, it seemed probable that fuming hydrochloric acid might be applied with advantage to this purpose; it would, however, be necessary to allow for the sugars formed from the starch and pentosans present. There would be no difficulty in this, as methods for estimating these substances with a fair degree of accuracy already exist. As the action of the fuming acid on starch and maltose has not yet been studied, a series of experiments was first made in this direction, and the results are here recorded. The velocity of hydrolysis of starch and maltose by fuming hydrochloric acid is dealt with in a separate paper (p. 2065).

When starch is left in contact, during several days, with dilute hydrochloric acid (7·5 per cent. HCl) it is converted, without dissolving, into the so-called "soluble starch"; when heated with very dilute hydrochloric acid for several hours, dextrose is formed. The latter process has been applied very widely as a means of estimating starch, although the fact that a considerable quantity of dextrose is destroyed renders such a method useless when any degree of accuracy is required (Davis and Daish, *J. Agric. Sci.*, 1914, **6**, 152). Early workers generally regarded the dextrose as formed directly from starch, and therefore looked upon the action of acids as essentially different from that of the enzyme diastase, the prolonged action of which on starch gives mainly maltose. Flourens, for instance (*Compt. rend.*, 1890, **90**, 1204), and Lintner and Düll (*Ber.*, 1895, **28**, 12) denied that maltose is formed at all by the

action of acids on starch. On the other hand, Weber and Macpherson (*J. Amer. Chem. Soc.*, 1895, 17, 312) showed the presence of considerable quantities of maltose in the commercial "glucose" manufactured by the action of acid on starch, whilst the analytical values obtained by Rolfe and Defren (*J. Amer. Chem. Soc.*, 1896, 18, 869) for starch transformations carried out in the autoclave with  $N/10$ - to  $N/1000$ -acids indicated the presence of 44 per cent. of maltose in a conversion carried to the point corresponding with that usual in the manufacture of "glucose," namely, when  $[\alpha]_D$  of the product is about  $129^\circ$ . The rest of the material seemed to consist of a mixture of dextrin and dextrose in nearly equal proportions. Rolfe and Haddock (*J. Amer. Chem. Soc.*, 1903, 25, 1015) subsequently isolated maltosazone from a starch transformation by acid, and quite recently Fernbach and Schoen (*Bull. Soc. chim.*, 1912, [iv], 11, 303) also isolated maltosazone from the product obtained by hydrolysing starch paste with different acids.\*

There is, therefore, at the present time, no reason for considering the action of acids on starch as essentially different from that of enzymes as regards the series of products formed. These are apparently soluble starch, dextrans, maltose, and dextrose. With ordinary diastase, maltose is the final product; with taka-diastase, which contains maltase, increasing quantities of dextrose are formed as the action proceeds, until a species of equilibrium is reached, when about 85 per cent. of dextrose and 15 per cent. of maltose are present (Davis and Daish, *loc. cit.*). The results now recorded, obtained with cold concentrated and fuming hydrochloric acid, may all be explained on similar principles. The main difference is, that with fuming hydrochloric acid the earlier stages, in which soluble starch, dextrin, and maltose are formed, are passed through very rapidly, so that, for example, with hydrochloric acid of  $D\ 1.210$ , 86 per cent. of the theoretical quantity of dextrose has been formed after so short a time as one hundred and thirty-five minutes. Maltose is hydrolysed to dextrose by the fuming acid not much more rapidly than starch itself; so that although acid of this concentration undoubtedly decomposes starch to maltose with extreme rapidity, the rate of production of dextrose is limited by the rate of hydrolysis of the maltose. As dextrose is formed, the specific rotatory power of the product falls continuously, until finally the value is the same as that of dextrose in acid of the same concentration. At the same time the reducing power gradually increases until it is the same as that of dextrose under the same conditions.

\* Kluver (*Biochemische Snijkerbepalingen*, Leiden, 1914) has made a series of analyses of commercial glucose syrups, prepared from starch, by the use of discriminating yeasts and finds from 15 to 20 per cent. of maltose to be present in such products.

When ordinary malt diastase is used to hydrolyse starch paste the dextrin stages are passed through relatively slowly; the amount of maltose formed progressively increases, but no dextrose is produced. With taka-diastase, however, dextrin disappears very rapidly, and even with small quantities of the enzyme (0.1 gram) after about three hours in the case of a 1 per cent. solution of starch, the product consists of maltose and dextrose only. As the dextrose increases in amount the maltose proportionately diminishes, so that there is little doubt that the former is produced at the expense of the latter. There is no evidence for the view that the dextrose is formed in these circumstances directly from the starch (compare Davis, *J. Soc. Dyers*, 1914, **30**, 249). In the same way the data obtained for the velocity of the action of fuming hydrochloric acid (p. 2065) are best interpreted by the view that the dextrose is formed from maltose produced as an intermediate product in the action.

Willstätter and Zechmeister (*loc. cit.*) have called attention to the extraordinarily high values of the specific rotatory power of dextrose obtained in fuming hydrochloric acid solutions. Thus when dextrose is dissolved in acid of D 1.210 after about twenty minutes,  $[\alpha]_D^{15-17} = 116.1^\circ$  ( $c=1.11$ ), the ordinary value for an aqueous solution of dextrose being  $[\alpha]_D^{15} 52.7^\circ$ . It is probable (Davis, *loc. cit.*) that this great change of rotation, which takes place with extreme rapidity, a nearly constant value being obtained after a few minutes, is due to the transformation by the fuming acid of the whole, or nearly the whole, of the dextrose into the  $\alpha$ -form, the specific rotatory power of which in aqueous solution is generally taken as about  $110^\circ$ . It has been shown recently that even in dilute aqueous solution the presence of neutral salts and of substances such as the alcohols, causes very considerable changes in the equilibrium existing between the two stereoisomeric forms of a hexose sugar (Walker, *Proc. Roy. Soc.*, 1913, *A*, **88**, 246; Worley, *ibid.*, 439). The effect of the fuming hydrochloric acid is apparently to convert the  $\beta$ -dextrose, with  $[\alpha]_D + 20^\circ$ , existing in the equilibrium mixture of  $\alpha$ - and  $\beta$ -dextrose which is present in an aqueous solution of dextrose ( $[\alpha]_D 52.7^\circ$ ), largely into the  $\alpha$ -form, having a high rotation.

Worley (T., 1911, **99**, 349) has drawn attention to one of the difficulties which arises in following exactly by means of the polarimeter the course of hydrolysis of polysaccharides by acids, owing to the dilute acid causing an alteration in the polarimetric end-point after the actual hydrolysis is complete. An example is given of a solution containing 1 molecular proportion of sucrose, 1 of hydrogen chloride, and 40 of water (approximately 50 per cent. sucrose

solution and 5 per cent. hydrochloric acid); the reading was found to rise after the lowest value was reached from  $161.20^\circ$  to  $161.335^\circ$  during about fifteen hours. With invert-sugar it might be thought that the rise of the reading is due to a destruction of the levulose present, as the latter is known to be readily destroyed by hydrochloric acid (compare Davis and Daish, *J. Agric. Sci.*, 1913, 5, 437). The experiments now recorded, however, show that a similar change takes place in dextrose even in a 1.11 per cent. solution of the sugar in the presence of concentrated or fuming hydrochloric acid. In spite of the low concentration of the sugar, the change is far greater than when dilute acid is used. Thus in acid of D 1.163, which gave a value for dextrose after ten minutes of  $[\alpha]_D^{20}$   $63.61^\circ$ , and after forty minutes  $[\alpha]_D^{20}$   $63.73^\circ$ , a value  $65.84^\circ$  was obtained after seventy-two hours. This change of rotation must be distinguished from the ordinary mutarotation change, which in concentrated acid is complete after a few seconds. As the rotation rises the reducing power of the solution falls, so that with ordinary hydrochloric acid after ninety-six hours it is 92.5 per cent. that of dextrose. A similar phenomenon is observed in the case of the fuming acid (D 1.201), but it is more difficult to follow, as in this case actual destruction of dextrose soon occurs (after about six hours), which masks the rise of rotatory power. The destruction becomes evident by the solution turning more or less yellow.

The rise in the specific rotatory power and the simultaneous diminution of reducing power of dextrose in the presence of hydrochloric acid is probably due to a synthetic action occurring, accompanied by the formation of a di-(or poly-)saccharide. Emil Fischer (*Ber.*, 1890, 23, 3687) obtained by the action of hydrochloric acid on a concentrated solution of dextrose a new glucobiose, to which he gave the name isomaltose. This was obtained when dextrose was dissolved in four times its weight of concentrated hydrochloric acid, and the mixture left for fifteen hours at  $10-15^\circ$ . The yield was 2.5 per cent. of the theoretical. More recently von Friedrichs (*Arkiv. Kem. Min. Geol.*, 1913, 5, No. 4), working under somewhat similar conditions, states that the product after twenty-four hours consists of 68 per cent. of dextrose, 18 per cent. of isomaltose, 8 per cent. of maltose, and 6 per cent. of unknown polysaccharides. In these experiments the sugar solutions were relatively concentrated. In those recorded in the present paper it is a striking fact that synthetic action still takes place, at the ordinary temperature, when the concentration of dextrose is so low as 1 per cent.

The gradual formation from dextrose under the influence of fuming or concentrated hydrochloric acid of a disaccharide having a higher rotatory power and a lower reducing power than dextrose

explains the fact that the hydrolysis of maltose or starch, when complete, calculated from the rotation, always seems greater by about 5 to 7 per cent. than when calculated from the reducing power. A similar fact was observed in the case of cellulose by Willstätter and Zechmeister, who, however, considered that in 1 per cent. solution of dextrose in fuming hydrochloric acid no isomaltose is formed, on finding that in such acid dextrose appeared to retain for more than forty hours the same specific rotatory power.\* This apparent constancy of the specific rotatory power is, however, due to the fact that the gradual destruction of dextrose (after twenty-five hours the solution has become decidedly yellow) masks the rise of the rotatory power which undoubtedly occurs (see p. 2058). The values given (below and pp. 2058, 2059) show very clearly that both with ordinary and fuming hydrochloric acid a rise of specific rotatory power of dextrose occurs, accompanied by a falling off of the copper reducing power. A certain amount of synthesis therefore occurs even in so low a concentration of dextrose as 1 per cent.

The fact that small quantities of a carbohydrate other than dextrose are formed by the action of fuming hydrochloric acid on cellulose and starch militates against the use of this acid as a means of quantitatively estimating cellulose even if actual destruction of dextrose were avoided.

#### EXPERIMENTAL.

##### *Specific Rotatory Power of Dextrose in Fuming Hydrochloric Acid* ( $D_{13}^{20}$ 1.210).

The fuming acid was prepared by saturating the ordinary concentrated hydrochloric acid with gaseous hydrogen chloride at 13°.

*Experiment 1.*—1.1100 Grams of anhydrous dextrose, dried in a vacuum at 105°, were dissolved in slightly less than 100 c.c. of the fuming acid, and the volume was made up to 100 c.c. at 15°. The sugar was completely dissolved in nine minutes. The solution was examined in a 2-dm. jacketted tube at 16.3° to 17°. The tube was closed with an indiarubber stopper to avoid loss of hydrogen chloride:

\* "Ueberraschend ist es, dass die Ausbeute an Glucose bei unserer Salzsäure-Methode nicht durch Bildung von Isomaltose herabgedrückt wird. Wir finden nun dass ihre Bildung nur in der von E. Fischer angewandten konzentrierten Glucose-Lösung erfolgt" (*Ber.*, 1913, 46, 2463). Ost (*Ber.*, 1913, 46, 2995) has suggested that with 3 per cent. or more of dextrose "reversion" to isomaltose might be expected in the presence of fuming hydrochloric acid; the results here given show that it actually occurs even in 1 per cent. solutions of dextrose.

Time after solution started, in minutes.	$\alpha_D$ .	$[\alpha]_D^{16-17}$
23 .....	2.578°	116.1°
360 .....	2.584	116.4

The reducing power of the solution was observed at intervals by diluting 10 c.c. portions of the solution with water, neutralising exactly with solid sodium carbonate, and treating with Fehling's solution under Brown, Morris, and Millar's conditions (T., 1897, 71, 72):

Time after solution started.	Mean CuO, gram.	Dextrose calculated, gram.	Dextrose found, per cent.
29 minutes .....	0.2747	0.1085	97.85
5 hours .....	0.2710	0.1070	96.4
23½ „ .....	0.2667	0.1052	94.7

After twenty-three and a-half hours the solution had become quite yellow, showing that decomposition of the dextrose had occurred.

*Experiment 2.*—1.9451 Grams of pure dextrose, dried in a vacuum at 105°, were dissolved in the fuming acid (D 1.210), and the volume was made up to 100 c.c. at 15°. The sugar was completely dissolved in fifteen minutes. The solution was examined in a 2-dm. tube at 16—16.5°:

Time after solution started, in hours.	$\alpha_D$ .	$[\alpha]_D^{16-16.5}$
1½ .....	4.459°	114.65°
4½ .....	4.453	114.44

Ten c.c. portions were withdrawn as before:

Time after solution started, in hours.	Mean CuO, gram.	Dextrose calculated, gram.	Dextrose found, per cent.
1½ .....	0.4457	0.1886	96.99
25½ (solution yellow) .....	0.4326	0.1812	93.2
39½ (solution quite yellow) .....	0.4304	0.1801	92.6

Care must be taken in the above experiments in neutralising the hydrochloric acid with sodium carbonate to avoid any considerable rise in temperature. If sodium hydroxide is used, the local development of heat generally brings about marked decomposition of the sugar.

*Experiment 3.*—A slightly less concentrated fuming hydrochloric acid was used (D<sup>15</sup> 1.201); 1.1111 grams of anhydrous dextrose were dissolved in the acid, and made up to 50 c.c. at 20°. The solution was examined in a 220-mm. tube at 20°:

Time from start.	$\alpha_D$ .	$[\alpha]_D^{20}$ .
15 minutes .....	4.660°	95.3°
3 hours .....	4.638	95.0
6½ hours .....	4.698	96.1

After six and a-quarter hours readings were not taken, as the decomposition of the sugar masked any rise in the specific rotatory power. It was at first thought that the low results obtained for the dextrose calculated from the values for the reducing power were due to an influence exerted on the latter by the large amount of sodium chloride present in the solution after neutralising the hydrochloric acid. Direct experiments were therefore made with a solution of dextrose, to which the same proportion of sodium chloride was added as was present in the actual solutions worked with (6.6 grams of sodium chloride in 100 c.c. during the reduction). It was found that the presence of the sodium chloride made no perceptible difference. Thus, for instance, when 0.1513 gram of dextrose was taken, 0.1502 gram of dextrose was found, or 99.3 per cent., a result almost within the limit of experimental error of the method.

From the above tables the extraordinary influence on the specific rotatory power of dextrose of a slight increase in the concentration of the fuming hydrochloric acid becomes apparent. Using acid of D 1.201 (39.3 per cent. HCl), the specific rotatory power of freshly dissolved dextrose is about  $95.5^\circ$ . With acid of D 1.210 (41.0 per cent. HCl) for a 1—2 per cent. solution, the specific rotatory power of dextrose may be taken as  $[\alpha]_D^{16-17} 115^\circ$ . It is very nearly constant during the short periods of one to two hours which are necessary to bring about complete hydrolysis of starch or maltose to dextrose, but even after one and a-quarter hours the values given above for the reducing powers show that marked synthetic action on the dextrose has actually occurred, and after three hours the rise of specific rotatory power shows that this change is still taking place. The following figures obtained with the ordinary concentrated hydrochloric acid (D<sup>15</sup> 1.163) show this action even more distinctly; with this strength of acid it is possible to follow the action for longer periods without marked decomposition of the dextrose occurring, such as masks the change in the case of the fuming acid.

*Action of Ordinary Concentrated Hydrochloric Acid (D 1.163)  
on Dextrose.*

*Series 1.*—1.1111 Grams of dextrose, dried in a vacuum at  $105^\circ$ , were dissolved in concentrated hydrochloric acid (D 1.163), and the volume made to 50 c.c. at  $20^\circ$ . The solution was examined in a 220-mm. tube at  $20^\circ$ :



Time from start.	$a_D$	$[\alpha]_D^{20}$
10 minutes .....	3.110°	63.61°
40 " .....	3.116	63.73
2 hours .....	3.118	63.77
48 " .....	3.217	65.80
72 " .....	3.219	65.84

*Series 2.*—5.0286 Grams of anhydrous dextrose were dissolved in concentrated hydrochloric acid (D 1.163), and the volume made up to 200 c.c. at 15°. The solution was examined in a 220-mm. tube at 15°. Portions of 25 c.c. each were withdrawn at intervals, neutralised with solid sodium carbonate, and made up to 200 c.c. at 15°, 50 c.c. portions being then taken for the reducing-power determinations (=0.1571 gram of dextrose):

Time from start.	$a_D$	$[\alpha]_D^{15.0}$	CuO from Dextrose		Dextrose, per cent.
			50 c.c., grams.	found, grams.	
34 minutes .....	3.482°	62.98°	0.3793	0.1553	98.85
23½ hours .....	3.612	65.31	0.3686	0.1506	95.85
47½ " .....	3.615	65.37	0.3619	0.1473	93.77
71½ " .....	3.627	65.58	—	—	—
95½ " .....	3.630	65.64	0.3580	0.1453	92.5

Even after ninety-six hours the solution had only just begun to show signs of decomposition, a faint yellow coloration being produced. With the fuming acid this occurs after twelve hours to a very marked degree.

#### *Action of Fuming Hydrochloric Acid on Starch.*

*Experiment 1.*—0.9276 Gram of purified potato starch, dried in a vacuum at 130° over phosphoric oxide, were dissolved in the fuming acid (D 1.210) and the volume made up to 100 c.c. at 15°. The starch very rapidly passed into solution, being first gelatinised and then dissolved. The solution was somewhat cloudy at first, but this soon cleared. The above weight of starch should yield 1.031 grams of dextrose.

The solution was examined in a 2-dcm. tube at 15.8—16.1°:

Time after solution started.	$a_D$	$[\alpha]_D^{16}$	Remarks.
17 hours .....	2.330°	113.00°	Solution yellow.

The reducing power of 10 c.c. was ascertained after eighteen hours:

Mean CuO, gram.	Dextrose found, gram.	Dextrose found, per cent.
0.2467	0.0970	94.1

*Experiment 2.*—1.9172 Grams of anhydrous starch were dissolved in slightly less than 200 c.c. of fuming acid at 15°, and the volume

was made up to exactly 200 c.c. at that temperature. The starch was completely dissolved in eighty minutes. The above weight of starch should yield 2.130 grams of dextrose. The solution was examined in a 2-dcm. tube at 15—16.3°:

Time after solution started, in minutes.	$\alpha_D$
85 .....	3.104°
114 .....	2.872
196 .....	2.580
319 .....	2.497
454 .....	2.473—solution becoming yellow.

Taking the value observed when the solution is first becoming yellow, namely, 2.473°, and calculating on the theoretical weight of dextrose, 2.130 grams, we have  $[\alpha]_D^{15-16.3}$  116.1°, which shows a practically complete conversion of the starch to dextrose.

*Experiment 3.*—2.4147 Grams of anhydrous starch were dissolved in fuming acid (D 1.210), and the volume was made up to 200 c.c. at 15°. The starch was completely dissolved in two hours. The above weight of starch should give 2.6835 grams of dextrose.

The solution was examined at intervals in a 220-mm. tube at 16—17°:

Time after solution started, in minutes.	$\alpha_D$
125 .....	3.861°
265 .....	3.459
400 .....	3.430—solution turning yellow.
605 .....	3.424

Taking the value observed of 3.430°, we have  $[\alpha]_D^{16-17}$  116.2°.

Portions of 10 c.c. each were withdrawn at intervals, neutralised with solid sodium carbonate, and the reducing power was determined:

Time after solution started, in minutes.	Mean CuO, gram.	Dextrose found, gram.	Dextrose, per cent.
135 .....	0.2770	0.1095	85.6
270 .....	0.3107	0.1240	92.44
410 .....	0.3135	0.1252	93.3
600 .....	0.3132	0.1251	93.23
1895 .....	0.3108	0.1240	92.44

The above experiments show that whereas the specific rotatory power of the product is practically identical ( $[\alpha]_D$  116°) with that of pure dextrose in hydrochloric acid of the same concentration, so that the conversion is practically 100 per cent., the value found or the latter from the reducing power of the product, calculated by the ordinary tables, is about 7 per cent. low. This is undoubtedly due, as explained above (p. 2057), to the action of the hydrochloric acid on the dextrose itself, giving rise to a di- or polysaccharide (isomaltose).

*Action of Fuming Hydrochloric Acid on Maltose.*

1.0363 Grams of maltose dried at 100—105° in a vacuum over phosphoric oxide were dissolved in fuming acid ( $D^{15}$  1.210), and the volume was made up to 100 c.c. at 15°. The sugar was completely dissolved in thirteen minutes. The above weight of maltose should give 1.094 grams of dextrose.

The solution was examined in a 2-dcm. tube at 15.5—16.5°:

Time after solution started, in minutes.	$\alpha_D$
22 .....	3.561°
77 .....	2.819
192 .....	2.541
357 .....	2.504
552 .....	2.484—solution turning yellow.

Taking the last value, we have  $[\alpha]_D^{15.5-16.5}$  113.55°.

Portions of 10 c.c. each were taken as before, and the reduction was estimated:

Time after solution started, in minutes.	Mean CuO, gram.	Dextrose found, gram.	Dextrose, per cent.
49 .....	0.2069	Maltose still present.	
573 .....	0.2635	0.1039	94.9

This experiment shows that maltose in 1 per cent. solution is almost as resistant to hydrolysis by fuming hydrochloric acid as starch itself under similar conditions, the action being complete after about six or seven hours at 15°. Exactly the same relationship between the specific rotatory power and reducing power of the product is observed as in the case of starch and dextrose.

*Action of Ordinary Concentrated Hydrochloric Acid on Starch.*

Pure hydrochloric acid ( $D^{15}$  1.163) was used (=32.1 per cent. HCl). The initial value of  $[\alpha]_D^{15}$  for dextrose (1.0401 grams in 100 c.c. of this acid) was found to be 63.55°; after forty-eight hours it was 65.8°.

*Experiment 1.*—3.5448 Grams of potato starch, dried in a vacuum at 130° over phosphoric oxide, were dissolved in concentrated hydrochloric acid ( $D^{15}$  1.163), and the volume was made up to 250 c.c. at that temperature. The greater part quite readily dissolved, but some starch was converted into a horny mass, which only dissolved slowly. All the starch was, however, dissolved in two hours. The above weight of starch should give 3.9390 grams of dextrose. The solution was examined in a 2-dcm. tube at 15.5—16.5°. The solution was quite clear:

Time after solution started, in hours.	$\alpha_D$ .	Time after solution started, in hours.	$\alpha_D$ .
17½ .....	3.137°	41 .....	2.147°
19½ .....	2.933	47 .....	2.119
22½ .....	2.671	49 .....	2.091
30 .....	2.344	90 .....	2.090

Taking the value 2.090° and calculating on 3.939 grams of dissolved solid (as dextrose), we have  $[\alpha]_D^{20}$  66.3°.

Portions of 10 c.c. each were withdrawn at intervals, neutralised with solid sodium carbonate, and the reducing power was determined:

Time after solution started, in hours.	Mean CuO, gram.	Dextrose found, gram.	Dextrose, Per cent.
17½ .....	0.2865	0.1135	72.04
23 .....	0.3204	0.1293	81.4
41½ .....	0.3581	0.1445	91.7
66½ .....	0.3642	0.1486	94.3
114 .....	0.3645	0.1488	94.4

*Experiment 2.*—2.0480 Grams of dry potato starch were dissolved in concentrated acid (D 1.163), and the volume was made up to 200 c.c. at 15°. The starch was slowly added to the acid so as to facilitate the solution, and was completely dissolved in sixty-five minutes. The above weight of starch should yield 2.2755 grams of dextrose.

The solution was examined in a 220 mm. tube at 15.5°—16.5°:

Time after solution started.	$\alpha_D$ .	Time after solution started,	$\alpha_D$ .
65 minutes .....	4.354°	31 hours .....	1.800°
4½ hours .....	3.896	47 .....	1.677
12 .....	2.685	73½ .....	1.682
23 .....	2.000	95½ .....	1.664
29 .....	1.842	120½ .....	1.646

Calculating for the reading after one hundred and twenty hours, we have  $[\alpha]_D^{16}$  65.7°. Portions of 10 c.c. each were taken as before, and the reducing power was determined:

Time after solution started.	Mean CuO, gram.	Dextrose found, gram.	Dextrose, per cent.
85 minutes .....	0.0360	0.0140	12.3
4½ hours .....	0.0984	0.0382	33.6
23 .....	0.2371	0.0930	81.7
48 .....	0.2711	0.1071	94.1
96 .....	0.2791	0.1104	97.0
122 .....	0.2772	0.1097	96.4

These two experiments show that after about fifty hours hydrolysis of the starch is complete (100 per cent.), the value obtained for the polarisation being the same as for dextrose in acid of the same concentration. The difference between the results by polari-

sation and reduction (about 6 per cent.) is again due to the formation of isomaltose. In experiment 2 the rotatory power remained constant between the forty-seventh and seventy-third hour, but subsequently destruction of the dextrose by the acid took place, and the solution became decidedly yellow (compare Ost, *Chem. Zeit.*, 1911, **35**, 1125).

Fuming hydrochloric acid (41 per cent. HCl) is seen to hydrolyse the starch more than ten times as rapidly as the ordinary concentrated acid.

*Action of more Dilute Hydrochloric Acid ( $D^{15}$  1.083;  
=16.7 per cent. HCl) on Starch.*

*Experiment 1.*—2.0564 Grams of dry potato starch were slowly added to about 200 c.c. of the acid at 15°. The starch was first gelatinised, and was dissolved in two and a-half hours. The above weight of starch should give 2.2849 grams of dextrose.

The solution was too opalescent at first to be examined in the polarimeter, but afterwards the following readings were taken in a 2-dm. tube at 15.5—16.5°:

Time after solution started, in hours.	$\alpha_D$ .	Time after solution started, in hours.	$\alpha_D$ .
22½ .....	4.117	118½ .....	3.920
46½ .....	4.092	173½ .....	3.785
72½ .....	4.012	192 .....	3.742

Portions of 10 c.c. were taken as before:

Time after solution started, in hours.	Mean CuO, gram.	Dextrose found, gram.	Dextrose, per cent.
3 .....	0.0028	—	—
22½ .....	0.0149	0.0058	5.0
47 .....	0.0163	0.0063	5.5
119 .....	0.0358	0.0139	12.1
191 .....	0.1171	0.0454	15.9

(from 25 c.c.)

Although the starch dissolves readily in hydrochloric acid of  $D$  1.083, the conversion into dextrose takes place extremely slowly, so that after forty-eight hours only about 5 per cent. of dextrose has been formed. The value of  $[\alpha]_D$ , calculated as starch from the reading after twenty-two and three-quarter hours, is 200.2°.

*Experiment 2.*—2.2708 Grams of dry starch were added to 200 c.c. of hydrochloric acid ( $D^{15}$  1.049=10 per cent. HCl), and the whole was kept at 15°. There appeared to be very little action on the starch, the latter not even being gelatinised. After four days the solution was filtered from the starch, and examined in a 4-dm. tube at 15.5—16.5°. The reading obtained was  $\alpha_D$  0.412°.

showing that very little starch had dissolved or been hydrolysed to dextrose.

Hence the limiting concentration of hydrochloric acid in which potato starch will readily dissolve at the ordinary temperature lies between D 1.083 and D 1.049.

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CXCII.—*The Velocity of Hydrolysis of Starch and Maltose by Cold Concentrated and Fuming Hydrochloric Acid.*

By ARTHUR JOHN DAISH.

THE velocity of hydrolysis of starch and maltose by cold concentrated and fuming hydrochloric acid has been studied polarimetrically at 20.00°; the results obtained throw an interesting light on the nature of the changes occurring during the hydrolysis of polysaccharides, and afford confirmation of the views put forward by Davis (*J. Soc. Dyers*, 1914, 30, 249) to explain certain abnormalities in the coefficient showing the velocity of action of enzymes on starch and maltose.

The great change of rotatory power which occurs when dextrose is dissolved in fuming hydrochloric acid is doubtless due to the transformation of  $\beta$ -glucose ( $[\alpha]_D^{19^\circ}$ ) (which constitutes about 63 per cent. of the equilibrium mixture existing in aqueous solution) into  $\alpha$ -glucose ( $[\alpha]_D^{110^\circ}$ ). Similarly, if the initial specific rotatory power of maltose in fuming hydrochloric acid is calculated from the curves given on p. 2071, before any hydrolysis has taken place, a value of  $[\alpha]_D^{20^\circ} = 157.4^\circ$  is obtained for acid of D<sup>15</sup> 1.201; for the ordinary concentrated acid in a similar manner a value  $[\alpha]_D^{20^\circ} = 141.0^\circ$  is obtained. When maltose is dissolved in water it shows mutarotation upwards, and after a short time equilibrium is established when  $[\alpha]_D^{20^\circ} = 137.6^\circ$ ; this solution probably contains a mixture of a  $\beta$ -glucose- $\alpha$ -glucoside ( $\beta$ -maltose) with  $[\alpha]_D^{114^\circ}$  and  $\alpha$ -glucose- $\alpha$ -glucoside ( $\alpha$ -maltose) with  $[\alpha]_D$  as yet unknown, but probably higher than 160°. The result of dissolving maltose in fuming hydrochloric acid is to shift the equilibrium existing between these two forms so as largely to increase the proportion of the  $\alpha$ -maltose of high rotatory power.

It has been suggested recently (Davis, *loc. cit.*) that the hydro-

lysis of polysaccharides, for example, starch and maltose, by enzymes, does not follow the simple unimolecular law of mass action, because the action occurring is not a single change, but is made up of a series of successive changes. Thus in the case of maltose three changes at least occur:

- (1)  $\beta\alpha$ -maltose  $\rightarrow$   $\alpha\alpha$ -maltose.
- (2)  $\alpha\alpha$ -maltose  $\rightarrow$  2 mols.  $\alpha$ -glucose.
- (3)  $\alpha$ -glucose  $\rightarrow$  equilibrium mixture of  $\alpha$ - and  $\beta$ -glucose.

The velocity of the main change (2), which is brought about by the enzyme, will, as a mass action, be modified by the velocity with which changes (1) and (3) occur; in the faintly acid or nearly neutral solutions in which enzyme actions take place, these changes take an appreciable time, so that the velocity-coefficient of the main change (2), when calculated by the ordinary unimolecular equation, is not a constant, but undergoes considerable variation during the course of the change.

When fuming hydrochloric acid is used to effect the hydrolysis of maltose the case is different. The greater part of the  $\beta\alpha$ -maltose is converted almost instantly into the form of higher rotatory power, so that immediately after the solution is made up the rotatory power has reached the high value  $[\alpha]_D^{20} 157.4^\circ$ .

After the hydrolysis of  $\alpha\alpha$ -maltose is complete the  $\alpha$ -glucose remains largely or completely in the  $\alpha$ -form, without undergoing change into the  $\beta$ -form. The consequence is that the disturbing effect of the changes (1) and (3) on the velocity of the main change is largely eliminated; this is made evident by the fact that during the whole of the hydrolysis of maltose by fuming acid the velocity-coefficient is practically a constant, varying only from 0.0103 to 0.0106, a variation which can be accounted for by experimental error. In this case a single change only occurs.

With ordinary hydrochloric acid, however, in which maltose dissolves as an equilibrium mixture not very different from that existing in aqueous solution ( $[\alpha]_D^{20} 141^\circ$  instead of  $137.6^\circ$ ), the effect of equation (1) on the velocity-coefficient of the total change becomes distinctly visible. A steady rise in the velocity-coefficient occurs, namely, from 0.00170 to 0.00186, a variation of about 10 per cent.

When the hydrolysis of starch by acid is considered, the series of changes is more complex. In order to avoid the difficulty that arises with ordinary starch owing to the appreciable time that elapses before the solid passes completely into solution, soluble starch was used throughout. Even when soluble starch is the starting point, several stages have to be passed through on the way to dextrose; dextrins and maltose are formed as intermediaries.

The result is that in the case of fuming hydrochloric acid the velocity-coefficient changes to a much greater extent than even with maltose and ordinary hydrochloric acid. There is a steady rise from 0.0052 to 0.0063, a range of variation of 23 per cent. With ordinary concentrated hydrochloric acid the variation of the coefficient is still greater, namely, from 0.00111 to 0.00144; the range is 30 per cent.

The transformation of cellulose into dextrose studied by Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401) affords an extreme instance of the departure of the law of action from the ordinary unimolecular law, owing to the occurrence of successive actions. On p. 2072 is given a table showing the results obtained by calculating from Willstätter and Zechmeister's data the value of the ordinary velocity-coefficient  $K = \log a/a - x$ . Fig. 1 shows the velocity curve. During the earlier period (the first two hundred minutes) this exhibits a double inflexion, and exactly corresponds in character with the curve of hydrolysis of starch to dextrose by means of taka-diastase (Davis and Daish, *J. Agric. Sci.*, 1914, **6**, 152); as in the latter case, the velocity-coefficient calculated for a unimolecular equation at first rises and then falls (Davis, *loc. cit.*). During this period the cellulose is transformed into a soluble polysaccharide, having no rotatory power, then into dextrin-like compounds, and finally into cellobiose; this substance, as shown by the experiments made with it by Willstätter and Zechmeister, is relatively slowly attacked by fuming hydrochloric acid. The latter part of the curve in Fig. 1 (from two hundred and fifty minutes to three thousand one hundred minutes) probably represents mainly the transformation of this sugar into dextrose; it is nearly logarithmic; but during the period 205—450 minutes, cellobiose is still being formed from the cellulose, so that there is a reinforcing effect on the ordinary mass action, and the coefficient rises from 0.000401 to 0.000536. Subsequently it becomes more constant for the rest of the transformation.

We have then, exemplified in the action of fuming and concentrated hydrochloric acids on starch and cellulose, the result of a series of successive and overlapping changes, the mathematical analysis of which would be of a highly complicated character. These changes show very great similarity to many cases of enzyme action, and justify the view put forward by Barendrecht (*Biochem. J.*, 1913, **7**, 548) and Davis (*loc. cit.*) that the departure of the law of action of enzymes in many cases from a simple unimolecular equation is due to the fact that in such cases a series of changes really occurs. When the subsidiary changes, which usually give rise to mutarotation effects, can, as in the case of



fuming acid and maltose, either be suppressed or rendered extremely rapid relatively to the main change, the action more and more closely approximates to the simple unimolecular law.

#### EXPERIMENTAL.

##### *Action of Fuming Hydrochloric Acid on Maltose.*

1.0555 Grams of carefully purified anhydrous maltose (dried in a vacuum at 105°,  $[\alpha]_D^{20}$  137.6° in 1 per cent. aqueous solution) were dissolved in fuming hydrochloric acid ( $D_{40}^{20}$  1.201); the volume was made up to 50 c.c. at 20°, and the solution examined in a 220-mm. tube at 20.00°.

When the velocity-coefficient is calculated from the ordinary unimolecular equation  $K = 1/t \log_{10} a/a-x$ , values ranging from 0.0094 to 0.0101 are obtained, the mean value being 0.0098.

This equation necessitates the use of an initial value corresponding with time  $t=0$ ; this was obtained as accurately as was possible by continuing the curve (Fig. 2) backwards, so as to cut the axis of  $t$ . As emphasised by Worley (T., 1911, 99, 352), any error in this initial value affects the accuracy of the whole series of values calculated for  $K$ . It is therefore preferable to calculate  $K$  from Worley's modified form of the equation:

$$K \log e = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2},$$

where  $a-x_1$  and  $a-x_2$  are the concentrations of sugar at times  $t_1$  and  $t_2$  respectively, the successive intervals of time being taken as small as the accuracy of the observations will allow or the rapidity of the change demands. This has been done in table I.

TABLE I.

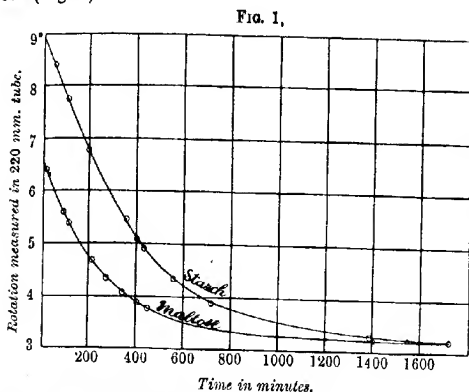
##### *Action of Fuming Hydrochloric Acid on Maltose at 20.00°.*

Time in minutes.	$a_t$ .	$a_t - a_\infty$ .	$K[\log e]$ .
0 .....	—	—	—
10 .....	6.85	2.16	—
15 .....	6.63	1.94	—
20 .....	6.43	1.74	—
25 .....	6.24	1.55	—
30 .....	6.07	1.38	—
35 .....	5.90	1.21	—
40 .....	5.75	1.06	0.0103
45 .....	5.63	0.94	0.0105
50 .....	5.53	0.84	0.0105
55 .....	5.44	0.75	0.0105
60 .....	5.36	0.67	0.0105
65 .....	5.28	0.59	0.0104
70 .....	5.20	0.51	0.0106
75 .....	5.14	0.45	0.0106
80 .....	5.08	0.39	{0.0111}
85 .....	5.02	0.33	—
90 .....	4.96	0.27	—
Final .....	4.69	—	—
			Mean . 0.0105

The values obtained for  $K$  by this method of calculation are probably more accurate than those obtained from the ordinary equation. It is seen that within the limits of experimental error the value of  $K \log e$  is constant.

*Action of Ordinary Concentrated Hydrochloric Acid on Maltose.*

1.0555 Grams of anhydrous maltose were dissolved in concentrated hydrochloric acid ( $D^{16} 1.163$ ), and the volume was made up to 50 c.c. at  $20^\circ$ . The solution was examined in a 220-mm. tube at  $20.00^\circ$  (Fig. 1).



Time in minutes.  
Action of concentrated hydrochloric acid ( $\Delta = 1.163$ ) on starch and maltose at  $20^\circ$ .

Calculating the value of  $K \log e$  by Worley's equation we have the following values for the velocity-coefficient.

TABLE II.

*Action of Concentrated Hydrochloric Acid on Maltose at  $20.00^\circ$ .*

Time in minutes.	$\alpha_t$	$\alpha_t - \alpha_\infty$	$K \log e$
0	—	—	—
50	5.97°	2.758°	—
100	5.49	2.278	—
150	5.09	1.878	—
200	4.76	1.548	—
250	4.47	1.258	(0.00170)
300	4.23	1.018	0.00174
350	4.04	0.828	0.00178
400	3.87	0.658	0.00186
450	3.75	0.538	0.00184
500	3.65	0.438	0.00183
550	3.57	0.358	0.00182
600	3.50	0.288	0.00179
650	3.44	0.228	0.00186
Final	3.212	—	—
Mean			0.00180

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The velocity-coefficient is clearly not constant. There is a steady rise in the value as time proceeds. For comparison, however, with the results with the fuming acid a mean value of  $K$  has been calculated. It is nearly constant during the latter stages of the action.

## *Action of Fuming Hydrochloric Acid on Soluble Starch.*

1.000 Gram of soluble starch ( $[\alpha]_D^{20} 198^\circ$ ,  $c=2$ ;  $R=1.0$ ) dried in a vacuum at  $130^\circ$  was dissolved in concentrated hydrochloric acid (D<sup>15</sup> 1.201), and the volume made up to 50 c.c. at  $20.0^\circ$ ; the solution was examined in a 220-mm. tube at  $20.0^\circ$  (curve, Fig. 2).

TABLE III.

## *Action of Fuming Hydrochloric Acid on Soluble Starch at $20.00^\circ$ .*

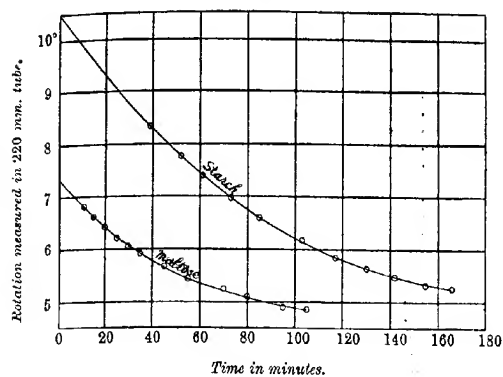
Time in minutes.	$a_t$ .	$a_t - a_\infty$ .	$K \log e$ .
0 .....	—	—	—
5 .....	10.20°	5.51°	—
10 .....	9.90	5.21	—
15 .....	9.61	4.92	—
20 .....	9.32	4.63	—
25 .....	9.05	4.36	—
30 .....	8.78	4.09	—
35 .....	8.64	3.85	0.0052
40 .....	8.30	3.61	0.0053
45 .....	8.07	3.38	0.0054
50 .....	7.85	3.16	0.0055
55 .....	7.64	2.95	0.0057
60 .....	7.43	2.74	0.0058
65 .....	7.24	2.55	0.0060
70 .....	7.06	2.37	0.0061
75 .....	6.89	2.20	0.0062
80 .....	6.73	2.04	0.0063
85 .....	6.59	1.90	0.0064
90 .....	6.46	1.77	0.0063
Final .....	4.69	—	—

In the case of soluble starch the velocity-coefficient is not constant, but rises continuously throughout the hydrolysis. The range of variation is about 20 per cent.

## *Action of Concentrated Hydrochloric Acid on Soluble Starch.*

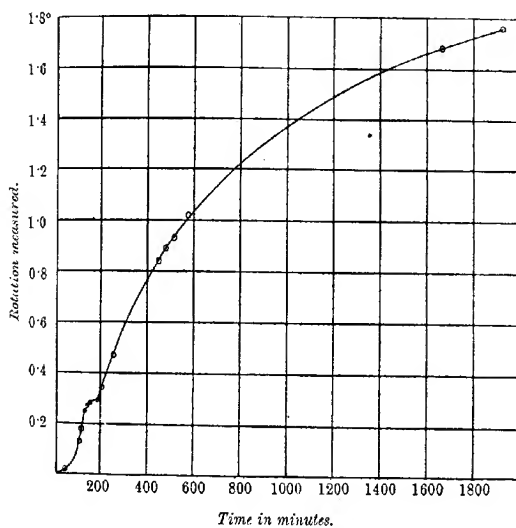
2.000 Grams of anhydrous soluble starch were dissolved in concentrated hydrochloric acid (D 1.163), and the volume was made up to 100 c.c. at  $20.0^\circ$ . The solution was examined in a 220-mm. tube at  $20.0^\circ$  (Fig. 3).

FIG. 2.



Action of fuming hydrochloric acid ( $\Delta=1.201$ ) on starch and mallose at  $20^\circ$ .

FIG. 3.



Action of fuming hydrochloric acid ( $\Delta=1.210$ ) on cellulose (Wülfstaller and Zechmeister).

TABLE IV.

*Concentrated Hydrochloric Acid on Soluble Starch at 20.0°.*

Time in minutes.	$a_t$ .	$a_t - a_{\infty}$ .	$K \log r$ .
0 .....	—	—	—
50 .....	8.34°	5.13°	—
100 .....	7.80	4.59	—
150 .....	7.25	4.04	—
200 .....	6.75	3.54	—
250 .....	6.29	3.08	0.00111
300 .....	5.86	2.65	0.00119
350 .....	5.47	2.26	0.00126
400 .....	5.09	1.88	0.00137
450 .....	4.80	1.59	0.00143
500 .....	4.57	1.36	0.00145
550 .....	4.37	1.16	0.00145
600 .....	4.20	0.99	0.00139
650 .....	4.05	0.84	0.00139
700 .....	3.92	0.71	0.00141
750 .....	3.80	0.59	0.00147
800 .....	3.72	0.51	0.00144
Final .....	3.21	—	—

The velocity-coefficient rises continuously throughout the change, the range being nearly 30 per cent.

TABLE V.

*Action of Fuming Hydrochloric Acid on Cellulose (Fig. 3).*

Velocity of hydrolysis for the whole action, calculated for the simple unimolecular equation, from Willstätter and Zechmeister's data.

Time in minutes.	$a_t$ .	$a_t - a_{\infty}$ .	$K = \frac{1}{t} \log \frac{a_0 - a_{\infty}}{a_t - a_{\infty}} \times 10^4$ .
0 .....	0.00°	1.97°	—
40 .....	0.02	1.95	113
105 .....	0.13	1.84	283
115 .....	0.18	1.79	362
130 .....	0.25	1.72	461
145 .....	0.27	1.70	442
155 .....	0.28	1.69	430
170 .....	0.29	1.68	407
185 .....	0.29	1.68	374
205 .....	0.34	1.63	401
255 .....	0.47	1.50	464
450 .....	0.84	1.13	536
480 .....	0.89	1.08	544
515 .....	0.93	1.04	539
575 .....	1.02	0.95	551
1665 .....	1.68	0.29	500
1925 .....	1.76	0.21	505
3100 .....	1.97	—	—

The velocity-coefficient rises to a maximum, then falls, and again rises and again falls.

TABLE VI.

*Action of Fuming Hydrochloric Acid on Cellulose.*

Velocity of hydrolysis during latter part of action, calculated by means of Worley's equation.

Time in minutes.	$\alpha_t$ (from curve).	$\alpha_t - \alpha_{\infty}$ .	$K \log e \times 10^6$ .
200 .....	0.335 <sup>5</sup>	1.635 <sup>5</sup>	—
300 .....	0.570	1.400	—
400 .....	0.760	1.210	—
500 .....	0.915	1.055	—
600 .....	1.040	0.930	—
700 .....	1.140	0.830	—
800 .....	1.225	0.745	—
900 .....	1.300	0.670	—
1000 .....	1.370	0.600	544
1100 .....	1.430	0.540	517
1200 .....	1.490	0.480	502
1300 .....	1.540	0.430	487
1400 .....	1.583	0.387	476
1500 .....	1.624	0.346	475
1600 .....	1.660	0.310	476
1700 .....	1.691	0.279	476
1800 .....	1.724	0.246	484
1900 .....	1.751	0.219	490
Final .....	1.970	—	—

The velocity-coefficient at first falls rapidly and then again rises.

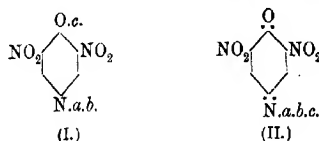
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CXCIII.—*Quinone-ammonium Derivatives. Part IV.*  
*Products of the Extreme Alkylation of Alkylated*  
*isoPicramic Acid.*

By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

IN the course of experiments having for their object the synthesis of quinone-ammonium derivatives containing an asymmetric quinquevalent nitrogen atom it has been shown that the third alkyl radicle may, in the case of *isopicramic acid*, attach itself to the oxygen of the hydroxyl group instead of to the nitrogen atom (this vol., p. 1469). Instead of the quinone-ammonium compound there would therefore be formed under these conditions an isomeric phenolic ether (*loc. cit.*, p. 1470). In view of this discovery it was pointed out in our last paper that a further study of the products of the extreme alkylation of the alkyl derivatives of *isopicramic*

acid under various conditions had become necessary, and we have accordingly carried out a series of experiments with mono- and di-methyl- and with mono- and di-benzylisopiramic acids, the complete alkylation of these compounds having been effected by means of methyl and ethyl sulphate respectively. The general result of these experiments is to show that in nearly all the cases studied the isomeric compounds I and II are formed simultaneously:

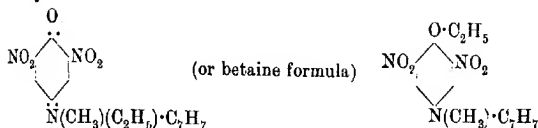


In confirmation of our former conclusion it appears, therefore, that when the nitrogen atom is weighted by a certain number of radicles heavier than methyl, further alkylation affects the hydroxyl group as well as the dialkylamino-group, notwithstanding the steric protection of the former. In the case of methyl alone, as made known in the first communication on the quinone-ammonium compounds (T., 1912, 101, 912), is the alkylation confined to the nitrogen atom, the hydroxyl group remaining unattacked under all conditions of methylation by methyl sulphate. When *a* and *b* are both represented by benzyl, the other extreme is reached, and alkylation is then restricted to the hydroxyl group, the phenolic ether being the sole product.

The phenolic ethers and the isomeric quinone-ammonium derivatives obviously belong to different types of compounds, and differ accordingly in their general characters. The former all crystallise in ochreous scales having much lower melting points than their isomerides; they are readily soluble in alcohol, and are possessed of but very feebly basic properties, some of them dissolving to a slight extent in concentrated hydrochloric acid to form salts which are immediately dissociated by water. The phenolic ethers are readily de-alkylated at the alkyloxy-group by heating with sulphuric acid diluted with a little water. Attempts to replace the nitro-groups in these compounds by reduction, and the application of the diazo-reaction according to the method which has given such successful results with the quinone-ammonium derivatives have invariably failed owing to the highly oxidisable character of the diamino-bases which rapidly give rise to resinous products. The quinone-ammonium compounds, unlike their isomerides, are distinctly basic, and can therefore be readily separated from the latter by acid extraction. They are but very sparingly soluble in alcohol, and resist de-alkylation by the sulphuric acid treatment; in the case

of benzyl only can the radicle be detached from the nitrogen atom by this treatment, but this decomposition can only be effected by the more violent action of practically concentrated sulphuric acid heated to its fuming point.

The formation of phenolic ethers instead of quinone-ammonium compounds was suspected, and referred to in our last paper (this vol., pp. 1473, 1481, and 1486). From the experimental part of this paper it will be seen that this suspicion has been fully justified, the compound containing, methyl, ethyl, and benzyl, for example (*loc. cit.*, p. 1486), having now been shown conclusively to be an ether, and not the quinone-ammonium derivative. At the same time a more exhaustive investigation of the method of alkylation has shown that the condition least favourable for the production of the quinone-ammonium compound is that the alkyl derivative to be subjected to extreme alkylation should be in the first place heated for some time in methyl or ethyl sulphate solution, and the reaction then completed by aqueous alkali in the usual way. Direct treatment of the alkyl derivative with methyl or ethyl sulphate and aqueous alkali as in the ordinary process in some cases favours the production of the quinone-ammonium compound at the expense of its isomeride. By taking advantage of this property of the alkyl sulphates we have now succeeded in preparing for the first time the quinone-ammonium compound containing an asymmetric quinquevalent nitrogen atom attached to the radicles methyl, ethyl, and benzyl:



The yield in this case is, however, small, the main product being the phenolic ether, 2:6-dinitrobenzylmethyl-*p*-phenetidine (see above formula), already described (*loc. cit.*, p. 1486).

The majority of the compounds which it has been found necessary to prepare for the present research have hitherto been undescribed, and their character and modes of preparation are given in the following section of this paper.

#### EXPERIMENTAL.

##### *Ethylation of Methylisopicramic Acid.*

Methylisopicramic acid (2:6-dinitro-4-methylaminophenol) was prepared from methyl-*p*-aminophenol by a modification of the process which has been found to give successful results in the



preparation of isopicramic acid (Meldola, Hale, and Thompson, *Chemical World*, 1912, 1, 327). As there is some difficulty in meeting the precise conditions necessary for the successful preparation of this compound the following details may be useful:

Methyl-*p*-aminophenol is converted into a diacetyl derivative by dissolving the substance in acetic anhydride, and, after the first reaction is over, adding a few drops of concentrated sulphuric acid and allowing the solution to remain for some hours at the atmospheric temperature. The product is precipitated by diluting the solution with water so as to decompose excess of acetic anhydride and partly neutralising with ammonia as the diacetyl derivative is somewhat freely soluble in dilute acetic acid. The crystalline diacetyl derivative is collected, washed with water, and then hydrolysed by dissolving in cold dilute sodium hydroxide solution, and precipitating by hydrochloric acid. By this treatment the *O*-acetyl is easily detached, and the phenolic monoacetyl derivative obtained. This compound crystallises from water in silvery scales melting at 245°. The nitration is best effected in small batches (2·5 grams) by suspending the crystalline compound in a little glacial acetic acid, and then adding gradually to the solution cooled in ice the necessary quantity (3 c.c.) of fuming nitric acid diluted with an equal volume of glacial acetic acid. The addition of the nitric acid causes the acetyl derivative to pass into solution, the beaker containing the latter being at this stage withdrawn from the ice-bath and allowed to remain for about an hour at the ordinary temperature. The solution is then poured on ice, and the product collected and washed with water. The dinitroacetyl derivative crystallises from dilute alcohol in ochreous scales, or on slow deposition in ochreous prisms, dissolving in aqueous alkali with an orange colour. The melting point is 142°—143°:

0·1015 gave 14·8 c.c.  $N_2$  (moist) at 20·5° and 752·8 mm.  $N=16·47$ .

$C_9H_9O_6N_2$  requires  $N=16·47$  per cent.

If the solution is kept too long at atmospheric temperature the whole product may be lost; on the other hand, by nitrating rapidly at a lower temperature with excess of fuming nitric acid a mononitro-compound has been obtained. In order to prepare the latter the acetyl derivative is as before suspended in glacial acetic acid, cooled in ice, and undiluted fuming acid added drop by drop with constant stirring until crystals begin to separate. After about fifteen minutes the solution is withdrawn from the ice-bath and poured on ice, when the mononitroacetyl derivative separates as a crystalline deposit. After being collected, washed, and crystallised from alcohol it consists of ochreous, nodular crystals, melting at 161°—162°:

0.1301 gave 15 c.c.  $N_2$  (moist) at  $19.5^\circ$  and 764.8 mm.  $N=13.30$ .  
 $C_9H_{10}O_4N_2$  requires  $N=13.33$  per cent.

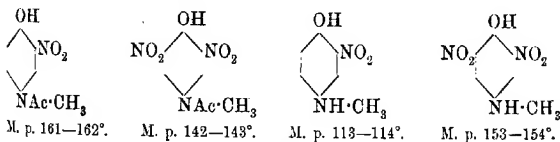
The mononitro-compound on further nitration gives the dinitro-derivative (m. p. 142–143°) described above. Both the mono- and di-nitro-derivatives are readily hydrolysed by heating with sulphuric acid diluted with a little water until a drop withdrawn from the solution ceases to show turbidity on dilution with water. The free base is precipitated by diluting the sulphuric acid solution with water and neutralising with ammonia or sodium hydroxide. The mononitro-compound prepared in this way is *2-nitro-4-methylaminophenol*; it crystallises from alcohol in dark reddish-brown scales, melting at  $113--114^\circ$ , and dissolving in dilute alkali with a crimson colour:

0.1002 gave 0.1832  $CO_2$  and 0.0450  $H_2O$ .  $C=49.86$ ;  $H=4.99$ .  
 0.0906 „ 13.1 c.c.  $N_2$  (moist) at  $17.5^\circ$  and 755.2 mm.  $N=16.63$ .  
 $C_7H_9O_3N_2$  requires  $C=49.97$ ;  $H=4.79$ ;  $N=16.67$  per cent.

The dinitro-compound obtained from its acetyl derivative by hydrolysis with sulphuric acid as above is *2:6-dinitro-4-methylaminophenol (methylisopicramic acid)*. It crystallises from alcohol in dark, slender, purple needles or scales according to the rate of deposition; the melting point is  $153--154^\circ$ , and the substance is very similar to *isopicramic acid* in its general properties, dissolving in aqueous ammonia with a purple colour and in dilute sodium hydroxide with a crimson colour:

0.1202 gave 21.2 c.c.  $N_2$  (moist) at  $19^\circ$  and 742.6 mm.  $N=19.79$ .  
 $C_7H_7O_5N_3$  requires  $N=19.72$  per cent.

The constitution of these compounds is determined by the following considerations: The dinitro-compound on being heated for a short time with benzyl chloride in presence of water gives benzylmethylisopicramic acid (m. p. 111–112°; this vol., p. 1484). As the mononitro-compound gives the dinitro-derivative on further nitration, the nitro-group in the former is in position 2 (or 6). The formulae are accordingly:



In view of the circumstance that the hydroxyl in methylisopicramic acid is most thoroughly “protected” by nitro-groups, this compound was used for further alkylation as being the more likely to yield quinone-ammonium derivatives. The substance was dis-

solved in excess of ethyl sulphate at  $100^{\circ}$ , and kept at this temperature for about an hour. The excess of ethyl sulphate was then decomposed by aqueous alkali in the usual way, and the crystalline deposit thus obtained was removed by filtration. The compound is extremely soluble in alcohol, and separates from a concentrated solution in flat, amber-coloured needles, melting at  $67-68^{\circ}$ ; it is slightly basic in character, dissolving in hydrochloric acid to a colourless solution, and separating in the original crystalline form on neutralising the solution with alkali. Analysis indicated that two ethyl groups had entered the molecule of methylisopiramic acid:

0.1004 gave 0.1794  $\text{CO}_2$  and 0.0526  $\text{H}_2\text{O}$ .  $\text{C}=48.73$ ;  $\text{H}=5.82$ .

0.1042 „ 13.9 c.c.  $\text{N}_2$  (moist) at  $17^{\circ}$  and 769 mm.  $\text{N}=15.66$ .

$\text{C}_{11}\text{H}_{15}\text{O}_5\text{N}_3$  requires  $\text{C}=49.04$ ;  $\text{H}=5.61$ ;  $\text{N}=15.62$  per cent.

The alkaline filtrate from which the above compound had been separated deposited in the course of some days another crop of crystals consisting of deep dull red needles having no melting point up to  $300^{\circ}$ , but blackening at about  $250^{\circ}$ . This compound is strongly basic, and more soluble in water than the substance described above; it separates but slowly from a concentrated solution in hydrochloric acid on the addition of alkali, and can be crystallised from boiling water, from which it is slowly deposited on cooling in orange prisms having a violet reflexion when in the mother liquor. The substance is but very sparingly soluble in alcohol, and this property, combined with its high melting point and strongly basic character, has led to the conclusion that it is the true quinone-ammonium compound. This conclusion is borne out by the analytical results, although the latter are complicated by the tendency of the compound to retain water of crystallisation:

0.1528 (originally deposited crystals dried at  $100^{\circ}$ ) gave 20.65 c.c.

$\text{N}_2$  (moist) at  $19.5^{\circ}$  and 762.7 mm.  $\text{N}=15.56$ .

$\text{C}_{11}\text{H}_{15}\text{O}_5\text{N}_3$  requires  $\text{N}=15.62$  per cent.

A specimen was prepared for combustion by dissolving in hydrochloric acid, neutralising with ammonia, and allowing to crystallise. The washed crystals, allowed to dry in a desiccator at the ordinary temperature, became opaque on drying at  $100^{\circ}$ , and lost water:

0.4278 lost 0.0264  $\text{H}_2\text{O}=6.17$ .

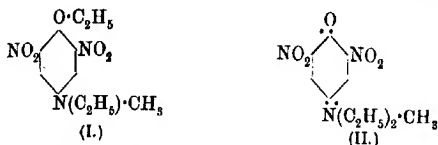
0.1324 (hydrate) gave 17.2 c.c.  $\text{N}_2$  (moist) at  $24^{\circ}$  and 765.1 mm.

$\text{N}=14.67$ .

$\text{C}_{11}\text{H}_{15}\text{O}_6\text{N}_3\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=6.27$ ;  $\text{N}=14.63$  per cent.

The combustions indicated that the specimen analysed may have retained a little more than the one molecule of water ( $\text{C}=45.02$ ;  $\text{H}=5.7$ ; instead of  $\text{C}=45.97$ ;  $\text{H}=5.97$  per cent.), but the general

results leave no doubt that the substance is the hydrated quinone-ammonium derivative. In this case, therefore, the ethylation of methylethylisopiramic acid resulted in the formation of the isomerides:

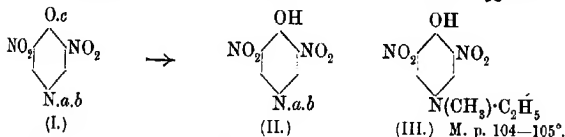


(I) 2:6-Dinitro-4-methylethylphenetidine.

(II) 2:6-Dinitro-4-methyldiethylammonium-1-benzoquinone.

Confirmation of this conclusion was obtained by de-alkylating the compounds by the sulphuric acid method previously described. The substance of low melting point (m. p. 67–68°) dissolves at once in concentrated sulphuric acid diluted with about one-fourth its volume of water, the solution then containing the sulphate of the base; this salt is dissociable by water, so that a drop of the solution diluted with water on a watch-glass gives an immediate yellow turbidity. On heating the acid solution for one or two minutes to its boiling point and allowing to cool, it no longer gives a turbidity on dilution with water, and the addition of alkali to the dilute solution causes the development of a purple colour, showing that de-alkylation has taken place. The compound of high melting point, on the other hand, remains unchanged under this treatment; it simply dissolves in the acid, and the solution, after being heated as above, on dilution and neutralisation with alkali, gives the original quinone-ammonium derivative.

The product obtained from the phenetidine derivative by de-alkylation showed, as had been anticipated, that the *O*-ethyl group had been removed, and that methylethylisopiramic acid had been formed. A general method for the synthesis of heterogeneous dialkyl derivatives of substituted *p*-aminophenol is thus suggested:



*Methylethylisopiramic Acid* = 2:6-dinitro-4-methylethylaminophenol (III above), prepared as described, can be obtained from the acid solution by neutralising with ammonia, the ammonium salt separating on cooling in characteristic bronzy scales. The free compound, liberated from the ammonium salt by dissolving the latter in hot water and neutralising with hydrochloric acid, has all

the properties of the dialkylisopicramic acid derivatives. It is both acid and basic, and forms an ammonium salt, which is but sparingly soluble in cold water, and dissolves in hot water with a purple colour. It dissolves freely in boiling alcohol, and crystallises from this solvent on cooling in dark brown scales with a bronzy lustre, and melting at 104–105°:

0.1017 gave 0.1668  $\text{CO}_2$  and 0.0439  $\text{H}_2\text{O}$ .  $\text{C}=44.73$ ;  $\text{H}=4.80$ .

0.1088 „ 17.35 c.c.  $\text{N}_2$  (moist) at 26.5° and 758.8 mm.

$\text{N}=17.61$ .

$\text{C}_9\text{H}_{11}\text{O}_5\text{N}_3$  requires  $\text{C}=44.78$ ;  $\text{H}=4.59$ ;  $\text{N}=17.43$  per cent.

It may be added that attempts to arrest the ethylation of methylisopicramic acid at the intermediate stage so as to obtain the above methylethyl derivative directly were unsuccessful, as two ethyl groups are introduced by ethyl sulphate under all conditions of alkylation. Dimethylisopicramic acid (T., 1912, 101, 924) can also be ethylated by the above process. The product is, no doubt, the phenolic ether (m. p. about 95°), but the yield is small, and no quinone-ammonium compound was obtained in this case.

#### *Ethylation of Benzylisopicramic Acid.*

In preparing benzylethylisopicramic acid by the ethylation of benzylisopicramic acid a non-phenolic by-product was obtained, which was provisionally regarded as the phenolic ether (this vol., p. 1485). A further supply of this compound has been prepared, and its properties studied more fully than was possible with the small quantity of material formerly at our disposal. The result of this later work is to confirm the conclusion that the substance is the phenetidine derivative, and not the quinone-ammonium compound.

The material required was prepared by dissolving benzylisopicramic acid in excess of ethyl sulphate at 100°, and keeping the solution at this temperature for about an hour. The product was then mixed with water, and the excess of ethyl sulphate removed by treatment with sodium hydroxide solution in the usual way. The crystalline deposit, after being collected and washed with water, was obtained by crystallisation from alcohol in lustrous, amber-coloured scales, melting at 129–130°:

0.1210 gave 0.2608  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C}=58.77$ ;  $\text{H}=5.42$ .

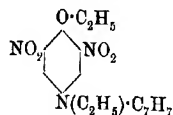
0.2033 „ 21.6 c.c.  $\text{N}_2$  (moist) at 15.5° and 751.4 mm.

$\text{N}=12.28$ .

$\text{C}_{17}\text{H}_{19}\text{O}_6\text{N}_3$  requires  $\text{C}=59.09$ ;  $\text{H}=5.54$ ;  $\text{N}=12.17$  per cent.

The compound is feebly basic, dissolving with difficulty in hot concentrated hydrochloric acid, and forming a solution which immediately becomes turbid on dilution with water owing to the

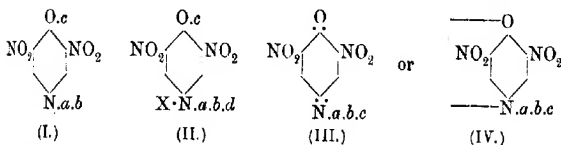
dissociation of the salt and the liberation of the free compound, which slowly separates in characteristic ochreous scales. The constitution of the compound is proved by its de-ethylation by sulphuric acid, with the formation of benzylethylisopicramic acid (this vol., p. 1485), melting at 96—97°, and the formula is accordingly:



2:6-Dinitro-4-benzylethyl-*p*-phenetidine.

The product of the extreme reduction of the above compound by tin and hydrochloric acid in the usual way was found, as in the case of all these phenolic ethers, to yield only resinous products when submitted to the diazo-reaction. The alkaline filtrate from which the original substance had been separated was concentrated by evaporation with the object of isolating any quinone-ammonium compound that might be formed. Nothing was deposited, however, on long keeping, and this derivative, if present, appears to be more soluble in water than its lower homologues. Such a compound, even if obtained, would be the benzyldiethyl derivative, and therefore of no special interest from the point of view of the present investigation.

A question of general interest in connexion with the phenolic ethers of the above type has been tested in the present case, but, so far, with negative results. A compound of the type (I) below contains a trivalent nitrogen atom, and might therefore be convertible into a compound containing an asymmetric quinquevalent nitrogen atom of the type (II). Some of the phenetidine derivative was therefore dissolved in excess of methyl sulphate and heated to

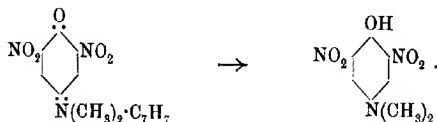


100° for an hour. After removal of the excess of methyl sulphate by alkaline treatment the substance was recovered unchanged, showing that no methylation had taken place. A similar result had been formerly obtained with dinitrodimethyl-*p*-anisidine (T., 1912, 101, 912), and it would appear that a free hydroxyl group in the para-position with the consequent possibility of assuming the "quinonoid" configuration (III) or (IV), is a condition essential to the formation of quinone-ammonium compounds. It is, of course,

possible that the nitro-groups may have some influence in checking the conversion of the tervalent into quinquivalent nitrogen in these phenolic ethers, and the experiments may be worth repeating with unsubstituted dialkyl-*p*-aminophenolic ethers if these compounds can be obtained with dissimilar radicles attached to the nitrogen atom. A compound of the required type, in which *a*, *b*, *c*, and *d* are all represented by methyl, namely,  $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \cdot \text{X}$ , is said to have been prepared by Griess (*Ber.*, 1880, **13**, 649), but there seems to be special difficulties connected with the formation of such compounds with dissimilar radicles in the "para" series.

*Methylation of Benzylopicramic Acid.*

A quinone-ammonium derivative obtained as a by-product during the methylation of benzylopicramic acid was described in our last paper (this vol., p. 1484). The substance is readily prepared in quantity by methylating benzylopicramic acid with excess of methyl sulphate in the presence of alkali in the usual way. A further study of its properties has confirmed the conclusion that it is a true quinone-ammonium compound; it has no definite melting point, but chars and decomposes at from 225° to 250°, according to the size of the crystals and the rate of heating. The compound is not decomposed by the sulphuric acid treatment if the solution is not too strongly heated, but if the acid is raised to near its boiling point the solution suddenly becomes turbid, and decomposition takes place with the formation of dimethylisopicramic acid (m. p. 182–183°; T., 1912, **101**, 924):



The constitution of the compound is established by this result, and, at the same time, the weakness of the attachment to the nitrogen atom of benzyl as compared with the true alkyls is strikingly revealed. The ready detachment of benzyl has been referred to before (this vol., p. 1481), and in the case of the present compound was again observed in the course of experiments on its products of reduction. A specimen was reduced by tin and hydrochloric acid in the usual way, and the acid solution, after removal of the tin as sulphide, concentrated by evaporation in order to obtain a diazotisable diamine. During the course of the evaporation a distinct odour of benzyl chloride was perceived, and resinous products were formed, from which nothing definite could be

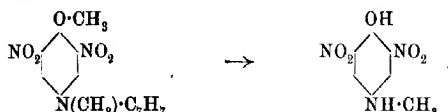
obtained. A similar result was observed on attempting to reduce fractionally with sufficient stannous chloride to reduce one of the nitro-groups, but the partial reduction of the compound requires further study, as derivatives of considerable interest might be obtainable by this method if it should prove experimentally realisable.

The main product of methylation of benzylisopicramic acid is the quinone-ammonium compound referred to above. There is simultaneously formed a small quantity of a less basic phenolic ether easily separable from its isomeride by the ready solubility of the latter in dilute hydrochloric acid. This compound, unlike the quinone-ammonium derivative, is readily soluble in alcohol, and crystallises in amber-coloured scales, melting at 75—76°:

0.0936 gave 10.9 c.c.  $N_2$  (moist) at 20.5° and 766.6 mm.  $N=13.41$ .

$C_{15}H_{15}O_5N_3$  requires  $N=13.25$  per cent.

This ether is also de-alkylated by the sulphuric acid treatment, losing both methyl and benzyl, with the formation of methylisopicramic acid:



#### *Methylation of Dibenzylisopicramic Acid.*

The distinctly basic character of the dimethylquinone-ammonium compound described in the preceding section suggested the possibility of directly methylating the mixture of mono- and di-benzyl derivatives of isopicramic acid obtained by the method of benzylation previously described (this vol., p. 1482). The tedious preliminary separation of the benzylated products would, it was anticipated, be rendered unnecessary by the conversion of the mono-benzyl derivative into the basic quinone-ammonium derivative, which is readily soluble in dilute hydrochloric acid, and could by this means be separated from less basic compounds. The isomeric phenolic ether, which in this case is formed only in very small quantity, was also expected to be more soluble than the corresponding dibenzyl-anisidine derivative, and therefore to be separable from the latter by crystallisation. These anticipations have been realised experimentally.

A mixture of mono- and di-benzylisopicramic acid was methylated by methyl sulphate and sodium hydroxide as before, and the product, after being collected and washed, extracted by warm dilute hydrochloric acid. The acid extract on neutralisation with ammonia



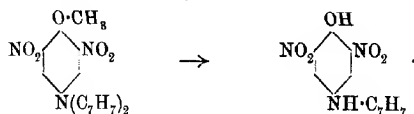
gave pure 2:6-dinitro-4-dimethylbenzylammonium-1-benzoquinone (found,  $N=13.32$ . calc.,  $N=13.25$  per cent.), so that the dibenzylisopiramic acid by this treatment apparently gives no quinone-ammonium compound.\* The less basic residue left after the acid extraction after two or three crystallisations from alcohol was obtained in dense, brown tablets, melting at  $97-99^\circ$ :

0.1056 gave 0.2471  $CO_2$  and 0.0448  $H_2O$ .  $C=63.81$ ;  $H=4.71$ .

0.1584 „ 15.2 c.c.  $N_2$  (moist) at  $22^\circ$  and 768.9 mm.  $N=11.0$ .

$C_{21}H_{19}O_5N_8$  requires  $C=64.09$ ;  $H=4.87$ ;  $N=10.69$  per cent.

The properties of the compound leave no doubt that it is the phenolic ether, 2:6-dinitro-4-dibenzylaminoanisole (2:6-dinitro-dibenzyl-*p*-anisidine). By the sulphuric acid treatment it parts with methyl and benzyl under all conditions, and gives monobenzylisopiramic acid (m. p.  $155-156^\circ$ ):



An attempt to replace the nitro-groups by reduction and the diazo-reaction resulted in the formation of the usual tarry products. The consideration of the form in which benzyl is detached from these compounds by the action of hot sulphuric acid is a point of some interest, which it is hoped may be made the subject of further investigation.

#### Ethylation of Benzylmethylisopiramic Acid.

The evidence on which was based the conclusion that the compound obtained by the ethylation of benzylmethylisopiramic acid is a phenetidine derivative and not a quinone-ammonium compound was given in our last paper (this vol., p. 1486). A further study of the substance in the light of later experience has confirmed this conclusion, and by the sulphuric acid treatment pure benzylmethylisopiramic acid has been obtained:



The complete reduction of the compound led to the formation

\* It may possibly be more soluble in water than the benzyl-dimethyl compound and therefore contained in the original alkaline mother liquor, but this has not yet been further examined.

of the oxidisable base obtained from all these phenolic ethers under similar conditions.

In view of the results obtained in the foregoing series of experiments a special search was made for the isomeric quinone-ammonium derivative by concentrating the alkaline filtrate from which the original phenolic ether had been removed by filtration. The solution deposited nothing on keeping for some days, but on being made strongly alkaline by sodium hydroxide an orange substance separated on stirring, and this, after being collected and washed, was found to possess all the properties of a quinone-ammonium compound, being distinctly basic in character. It was purified by solution in hydrochloric acid and precipitation by sodium hydroxide, and was obtained as an orange, microcrystalline powder, having, when dry, a decomposing point of about 191—193°:

0.0610 gave 6.75 c.c.  $N_2$  (moist) at 28° and 760.1 mm.  $N=12.48$ .

$C_{16}H_{17}O_5N_8$  requires  $N=12.68$  per cent.

The compound is accordingly the required 2:6 *dinitro-4-benzyl-methylethylammonium-1-benzoquinone*. Like all these quinone-ammonium compounds the substance is practically insoluble in alcohol, but is soluble in hot water. It appears from the cases so far studied that the solubility of these compounds in water increases with the weight of the radicles attached to the nitrogen atom. The main product of the ethylation is, however, in this case the phenetidine derivative, and we have had but a very small quantity of the quinone-ammonium compound at our disposal. The research will be continued with the object of increasing the yield if possible, so as to obtain sufficient material for an attempt to resolve the compound into optical isomerides.

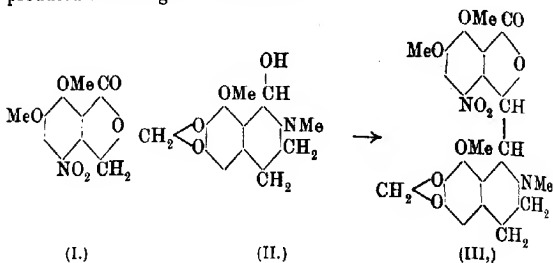
CITY AND GUILDS OF LONDON INSTITUTE;  
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#### CXCIV.—*Synthetical Experiments in the Group of the isoQuinoline Alkaloids. Part IV. The Synthesis of $\beta$ -Gnoscopine.*

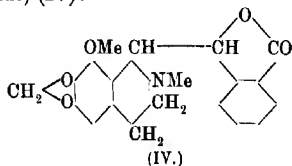
By EDWARD HOPE and ROBERT ROBINSON.

DURING the course of experiments instituted some three years ago with the object of discovering practical methods for the synthesis of alkaloids of the hydrastine and narcotine type, the authors observed that nitromeconine (I) and cotarnine (II) condense together with

extraordinary facility in alcoholic solution, yielding in almost quantitative amount a base, anhydrocotarninenitromeconine (III). This new base was believed to be nitrognoscopine (nitro-*r*-narcotine) produced according to the scheme\*:



As it had been found possible to obtain numerous condensation products of hydrastine and cotarnine with substances containing a nitro-group, the elimination of this group became a matter of importance, and in Part I of this series (T., 1911, **99**, 1153) we have described a method by means of which anhydrocotarninenitrophthalide may be converted into anhydrocotarninephthalide (dideoxygnoscopine) (IV):



In the experimental portion of the present communication it is shown that the nitro-group in anhydrocotarninenitromeconine may be similarly eliminated, by successive conversion into  $\cdot\text{NH}_2$ ,  $\cdot\text{NH}\cdot\text{NH}_2$ ,  $\cdot\text{H}$ , or alternatively into  $\cdot\text{NH}_2$ ,  $\cdot\text{I}$ ,  $\cdot\text{H}$ . The product is an optically inactive base,  $\text{C}_{22}\text{H}_{23}\text{O}_7\text{N}$ , melting at  $180^\circ$ , isomeric, but not identical with gnoscopine. The reactions of the new compound are precisely similar to those of narcotine and gnoscopine; thus it behaves as a lactone, can be converted into nornarceine and narceine (this being the most convenient synthesis of the latter alkaloid), and on oxidation yields cotarnine and opianic acid.

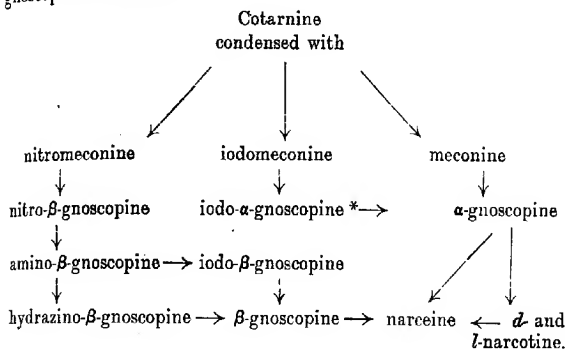
The arguments, then, which are used to establish the constitution of narcotine can equally be applied to the deduction of the same formula for the new base, and it is clear that this new compound is a stereoisomeride of narcotine and gnoscopine. It is proposed

\* The mechanism of this and similar condensations has been described in a previous communication (T., 1911, **99**, 2117).

to call the substance melting at  $180^{\circ}$   $\beta$ -gnoscopine, reserving the name  $\alpha$ -gnoscopine for the compound previously known as gnoscopine or *r*-narcotine, which melts at  $229^{\circ}$ . A partial conversion (see p. 2101) of  $\beta$ -gnoscopine into  $\alpha$ -gnoscopine occurs when the base is heated for a long period in aqueous alcoholic solution at  $100^{\circ}$ .

Stereoisomerism is observed not only in the case of  $\alpha$ - and  $\beta$ -gnoscopines, but also in the case of their iodo-derivatives, iodo- $\alpha$ -gnoscopine, and iodo- $\beta$ -gnoscopine, which yield  $\alpha$ - and  $\beta$ -gnoscopines respectively on reduction with aluminium amalgam in alcoholic solution.

The following table illustrates the relations of the various gnoscopine derivatives:



Of the three methods of obtaining  $\alpha$ -gnoscopine indicated in this table, that through iodo- $\alpha$ -gnoscopine is by far the most convenient, whilst  $\beta$ -gnoscopine and narceine are best obtained through hydrazino- $\beta$ -gnoscopine.

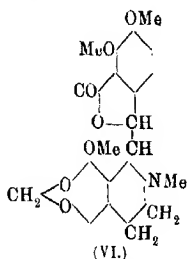
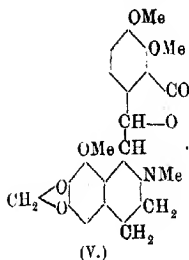
The interesting question regarding the nature of the stereo-isomerism of  $\alpha$ - and  $\beta$ -gnoscopine has engaged our attention, but we are at present unable to go beyond speculation and suggestion. The stereo-isomerism persists, as seen above, through a series of derivatives, and survives the opening of the lactone ring. The two dissimilar asymmetric carbon atoms which  $\alpha$ - and  $\beta$ -gnoscopines contain would obviously account for the existence of two inactive forms of gnoscopine (as in the case of  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid), and would further require the existence of four optically active modifications.  $\alpha$ -Gnoscopine has already been resolved into its optically active components,  $d$ - and  $l$ -narcotine, by Perkin and Robinson (T., 1911, 99, 775), but our efforts to resolve  $\beta$ -gnoscopine

\* Perkin and Robinson, T., 1911, 99, 775.

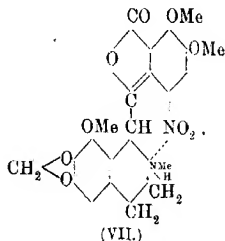
or one of its substitution products have so far failed. In some preliminary attempts to resolve  $\beta$ -gnoscopine, using *d*-bromocamphorsulphonic acid, it was not found possible to obtain a crystalline salt. Later, experiments were made with a view to obtain complex salts like morphine  $\beta$ -gnoscopine sulphate and morphine  $\beta$ -gnoscopine sulphosalicylate. The fractional crystallisation of these salts did not, however, give any satisfactory result. A more prolonged investigation of these salts than is considered necessary for the present communication will evidently be required before  $\beta$ -gnoscopine can be resolved with their aid.

Experiments have been made also to obtain evidence of the asymmetry of the  $\beta$ -gnoscopine molecule by fractionally crystallising (a) the condensation product of amino- $\beta$ -gnoscopine with *d*-hydroxymethylenecamphor (compare Pope and Read, T., 1909, 95, 171; 1913, 103, 444), and (b) the condensation product of hydrazino- $\beta$ -gnoscopine with *L*-menthone. In the case of the first of these, the condensation product is obtained in almost quantitative amount, and on careful fractional crystallisation a definite substance having  $[\alpha]_D +150^\circ$  and melting at  $137\text{--}138^\circ$  is obtained in an amount closely approaching 50 per cent. of the crude product. This is probably one of the expected isomerides, but it must be pointed out that it has proved impossible, working with the quantity recorded (p. 2094), to isolate in reasonable amount, the expected isomeride. A final decision regarding the exact nature of the substance melting at  $137\text{--}138^\circ$  has not been arrived at because of the impossibility of obtaining the free amine from it. In the case of the menthone condensation product (p. 2097), which is obtainable in about 70 per cent. yield, repeated crystallisation produces a gradual change in the rotatory power, but it is evident that the separation of the isomerides (if the change of rotation may be interpreted in this way) is not sufficiently sharp to render the method a practicable one for the preparation of an optically active  $\beta$ -gnoscopine.

Although the ordinary stereochemical explanation of the isomerism of  $\alpha$ - and  $\beta$ -gnoscopines is probably the correct one, it may be pointed out that there are at any rate two other ways of accounting for isomeric gnoscopines. In the first place, in view of the recent work of Cain, Coulthard, and Micklethwait (T., 1912, 101, 2298), it is possible to assume the absence of free rotation of the bond joining the meconine nucleus to the hydrocotarnine residue. In that case  $\alpha$ - and  $\beta$ -gnoscopine might be represented by V and VI respectively:

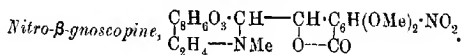


Some justification for this view may be derived from the interesting fact that nitro- $\beta$ -gnoscopine possesses intense visible colour. Both nitromeconine and  $\alpha$ - and  $\beta$ -gnoscopines are colourless, so that the yellow colour of nitro- $\beta$ -gnoscopine must be ascribed to the mutual influence of the nitro- and  $\cdot$ NMe-groups. The attraction between these groups may not find expression in a complete bond as in the quinonoid formula (VII), but it probably involves a proximity of the negative nitro- and the positive  $\cdot$ NMe-groups in the molecule:



In the second place, if it be assumed that the valencies of the nitrogen atom are not all in one plane, then, obviously, the methyl group attached to the nitrogen atom may be in the *cis*- or *trans*-position with respect to the meconine complex. If either the first or the second of these possible causes operates in addition to the ordinary stereochemical cause, there should be eight active isomerides and four inactive isomerides, whilst if both so operate there should be sixteen active and eight inactive isomerides.

#### EXPERIMENTAL.



Nitromeconine (5 grams) is dissolved in boiling alcohol (150 c.c.) and cotarnine (5 grams) added, either in the solid condition or in

alcoholic solution. The solution becomes orange-brown, and a bright yellow, granular precipitate soon separates. The reaction is complete after boiling for ten minutes. After cooling, the product is collected, washed with alcohol, and dried. When obtained in this way, the nitro- $\beta$ -gnoscopine was in an almost pure condition, the yield being about 90 per cent. of that theoretically possible. Nitro- $\beta$ -gnoscopine is very sparingly soluble in ethyl and methyl alcohols, and in most other organic solvents, but can be conveniently crystallised from trichloroethylene, from which it separates in canary-yellow prisms, melting at  $191^{\circ}$ :

0.1819 gave 0.3821  $\text{CO}_2$  and 0.0760  $\text{H}_2\text{O}$ .  $\text{C}=57.3$ ;  $\text{H}=4.7$ .

$\text{C}_{22}\text{H}_{22}\text{O}_6\text{N}_2$  requires  $\text{C}=57.6$ ;  $\text{H}=4.8$  per cent.

The substance is a true base, and forms salts with acids. It dissolves in glacial acetic acid in the cold, and when the solution is diluted, no precipitate is obtained. On adding picric acid to the solution in acetic acid an orange-yellow precipitate is obtained, which may be crystallised from methyl ethyl ketone, in which it is very sparingly soluble. This substance melts and decomposes at  $153^{\circ}$ , and is evidently the *picrate* of nitro- $\beta$ -gnoscopine. If, however, the solution in glacial acetic acid or in dilute acetic acid is boiled, decomposition to nitromeconine and cotarnine occurs. Thus a solution of the base (2 grams) in acetic acid (10 c.c.) was boiled for two minutes, and, whilst hot, diluted with an equal volume of water. The needles which separated on cooling were readily identified by their melting point ( $160^{\circ}$ ) as nitromeconine—the melting point of a mixture with pure nitromeconine being also  $160^{\circ}$ . On adding picric acid to the filtrate from the nitromeconine, cotarnine picrate was produced, and this when crystallised from water melted at  $139^{\circ}$  (Salway, T., 1910, **97**, 1209).

*Hydrochloride*.—The bright yellow base dissolves in concentrated hydrochloric acid to a pale yellow solution, which on dilution with water furnishes after some time a crystalline precipitate consisting of pale yellow prisms, soluble in much water. On treating with ammonia, nitro- $\beta$ -gnoscopine is regenerated:

0.1200 gave 0.0373  $\text{AgCl}$ .  $\text{Cl}=7.6$ .

$\text{C}_{22}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{HCl}$  requires  $\text{Cl}=7.1$  per cent.

This substance melts and decomposes at  $142$ – $143^{\circ}$  to a red liquid, and on boiling with water yields nitromeconine and cotarninum chloride.

*Aurichloride*.—This derivative is obtained by the addition of gold chloride to a solution of nitro- $\beta$ -gnoscopine in excess of dilute hydrochloric acid. It is an amorphous, yellowish-brown precipitate, becoming crystalline on keeping. It begins to darken and decompose at  $160^{\circ}$ , violent decomposition occurring at  $170^{\circ}$ :

0.1297 gave 0.0316 Au. Au=24.4.

$C_{22}H_{22}O_9N_2HAuCl_4$  requires Au=24.8 per cent.

The *platinichloride* is similarly obtained in yellow needles.

*Methiodide*.—Nitro- $\beta$ -gnoscopine dissolves in boiling methyl iodide, and soon a new substance crystallises from the solution in prismatic needles. Great difficulty was experienced in recrystallising this compound. It has a pale yellow colour, and melts and decomposes at 204–206°. It is very sparingly soluble in water or alcohol:

0.1214 gave 0.0485 AgI. I=21.4.

$C_{22}H_{22}O_9N_2CH_3I$  requires I=21.0 per cent.

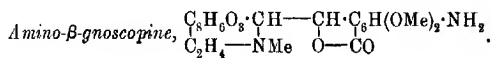
#### *Nitronarceine.*

Nitro- $\beta$ -gnoscopine methiodide was warmed with water, and excess of freshly precipitated silver chloride on the water-bath, and the resulting solution filtered and cooled. On the addition of dilute potassium hydroxide solution an orange precipitate of an ammonium hydroxide was formed, and this was collected, washed with water, and boiled with excess of water. The orange substance first became yellow, and then passed into solution. On concentrating, nitronarceine separated in orange-coloured, leaf-shaped microcrystals, melting at 160–170°, and decomposing at a higher temperature:

0.1162 \* gave 5.7 c.c.  $N_2$  at 19° and 765 mm. N=5.8.

$C_{23}H_{26}O_{10}N_2$  requires N=5.7 per cent.

*Nitronarceine* is rather sparingly soluble in hot water, but dissolves in solutions of either acids or alkalis. Its *potassium* salt crystallises in pale yellow prisms when a hot concentrated solution of the base in potassium hydroxide is cooled. Unlike narceine, the substance in the solid state gives no coloration with iodine.



In the preparation of this substance, nitro- $\beta$ -gnoscopine (10 grams) is dissolved in 50 c.c. of glacial acetic acid. A few pieces of granulated tin are added, and then a solution of 25 grams of hydrated stannous chloride in 30 c.c. of concentrated hydrochloric acid, the temperature being carefully kept below 15°. After the solution has remained for six hours, during which time the yellow colour disappears, water is added in sufficient quantity to redissolve the precipitate of the stannichloride at first produced. Then excess of concentrated sodium hydroxide solution is added, and the result-

\* Dried at 100°.



ing alkaline solution extracted with chloroform. As much of the chloroform solution as possible is run off from the mixture, and the remaining partial emulsion shaken with more chloroform. The combined extracts are dried with potassium carbonate, and the chloroform distilled. When almost all the solvent is removed and the substance begins to crystallise, methyl alcohol is added and the distillation continued until very little chloroform remains. On allowing the liquid to cool, the product crystallises out almost completely. After collecting and washing with alcohol, it is in a practically pure condition, the yield being about 75 per cent. of that theoretically possible. The amine crystallises well from ethyl acetate in colourless, glistening prisms, melting at  $205^{\circ}$ . It also crystallises readily from a mixture of chloroform and benzene:

0.1490 gave 0.3369  $\text{CO}_2$  and 0.0727  $\text{H}_2\text{O}$ .  $\text{C}=61.6$ ;  $\text{H}=5.4$ .

$\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}_2$  requires  $\text{C}=61.6$ ;  $\text{H}=5.6$  per cent.

*Amino- $\beta$ -gnoscopine* is readily soluble in chloroform or pyridine, sparingly so in benzene, alcohol, or ethyl acetate, and very sparingly soluble in ether or light petroleum. Its salts with acids are all readily soluble in water. The solution of amino- $\beta$ -gnoscopine in glacial or dilute acetic acid or dilute hydrochloric acid is not changed on boiling. On the addition of platinic chloride, gold chloride, or mercuric chloride to the solution of the hydrochloride, precipitates were obtained which were apparently amorphous. The amine is easily diazotised in dilute hydrochloric acid solution, but the diazo-solution quickly becomes orange, and finally reddish brown. This decomposition was not noticed in the case of diazo-solutions prepared in concentrated hydrochloric acid solution. The diazo-compound yielded with alkaline  $\beta$ -naphthol an azo-compound of intense crimson colour, which dissolved in concentrated sulphuric acid to a deep blue solution. On dissolving the amine in excess of methyl iodide and boiling the solution for a short time, crystallisation of a methiodide occurs at a certain stage, on allowing some of the methyl iodide to escape. The substance so obtained is crystalline, but of indistinct form. It contains only one iodine atom (Found,  $\text{I}=19.0$ ;  $\text{C}_{23}\text{H}_{27}\text{O}_7\text{N}_2\text{I}$  requires  $\text{I}=22.2$  per cent.). The compound appears to contain the amino-group, since it yields a diazonium salt on treatment with dilute hydrochloric acid and sodium nitrite. This combines with  $\beta$ -naphthol, giving a scarlet azo-dye.

*Acetyl-amino- $\beta$ -gnoscopine*.—This derivative is readily obtained by the addition of acetic anhydride to a solution of the base in acetic acid. After allowing to remain for an hour at the ordinary temperature, water is added to the mixture, and the acetyl compound precipitated with ammonia. It is readily soluble in hot

alcohol, and separates, on cooling, in highly characteristic bunches of needles melting at  $198^{\circ}$ . If the crystallisation is allowed to occur slowly, the crystals separate as prisms. This derivative dissolves readily in dilute hydrochloric acid, and the solution is unchanged on the addition of sodium nitrite:

0.1204 gave 0.2697  $\text{CO}_2$  and 0.0597  $\text{H}_2\text{O}$ .  $\text{C}=61.4$ ;  $\text{H}=5.5$ .

$\text{C}_{24}\text{H}_{28}\text{O}_8\text{N}_2$  requires  $\text{C}=61.3$ ;  $\text{H}=5.5$  per cent.

*Phenylcarbamido- $\beta$ -gnoscopine*,  $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ .

In the preparation of this derivative, phenylcarbimide (2 grams) is warmed for ten minutes with amino- $\beta$ -gnoscopine (1 gram) and sufficient benzene to cause solution of the amine. After concentrating and cooling the solution, colourless, prismatic needles separate, and these, after recrystallisation from alcohol (in which they are sparingly soluble), melt at  $208^{\circ}$ , decomposing to a dark red liquid:

0.1231 gave 0.2863  $\text{CO}_2$  and 0.0607  $\text{H}_2\text{O}$ .  $\text{C}=63.4$ ;  $\text{H}=5.5$ .

$\text{C}_{22}\text{H}_{20}\text{O}_8\text{N}_2$  requires  $\text{C}=63.6$ ;  $\text{H}=5.3$  per cent.

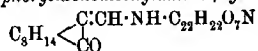
This substance dissolves in very dilute hydrochloric acid, but its solution in the more concentrated acid, although readily formed, soon deposits crystals of a sparingly soluble *hydrochloride*.

*Succinimino- $\beta$ -gnoscopine*,  $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}\cdot\text{N} \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$

Molecular proportions of amino- $\beta$ -gnoscopine and succinic anhydride are boiled together for about four hours in chloroform solution. The product is isolated by evaporating the chloroform and adding methyl alcohol as soon as signs of crystallisation appear. The product can be conveniently recrystallised from a mixture of chloroform and methyl alcohol. The crystals are faintly yellow, and melt at  $248\text{--}250^{\circ}$ . This substance is practically insoluble in benzene, light petroleum, or ether, and sparingly soluble in ethyl acetate, methyl alcohol, or ethyl alcohol. It is insoluble in aqueous alkaline hydroxides even on boiling, but the ring (either phthalide or succinimide ring, or both) is broken by alcoholic potassium hydroxide. It is readily soluble in dilute hydrochloric acid, and can be precipitated by careful addition of dilute potassium hydroxide, but the addition of excess apparently ruptures the ring, for the precipitate redissolves:

0.1370 gave 0.3097  $\text{CO}_2$  and 0.0648  $\text{H}_2\text{O}$ .  $\text{C}=61.6$ ;  $\text{H}=5.2$ .

$\text{C}_{22}\text{H}_{20}\text{O}_9\text{N}_2$  requires  $\text{C}=61.2$ ;  $\text{H}=5.1$  per cent.

*d*-Camphorylidene-methylamino- $\beta$ -gnoscopine,

As already stated in the introduction (p. 2088), this compound was prepared in the hope that it would afford evidence of the asymmetry of the  $\beta$ -gnoscopine molecule. It is readily obtained by mixing a solution of amino- $\beta$ -gnoscopine (4.28 grams) in 60 per cent. acetic acid (14 c.c.) with *d*-hydroxymethylenecamphor\* (1.8 grams) in alcohol (4 c.c.). The reaction is complete after heating for half an hour on a steam-bath. On pouring the mixture into water and adding dilute potassium hydroxide solution a canary-yellow precipitate of the condensation product is formed. The yield of crude dry substance is 5.4 grams, that is, about 90 per cent. of that theoretically possible. On crystallising the crude material from methyl alcohol and subsequently evaporating the mother liquors several fractions were obtained, the rotatory powers and melting points of which were observed. These results are summarised in the following table. In the determination of the optical activity about 0.1 gram of substance was dissolved in 10 c.c. of chloroform:

The crude material (total weight 5.4 grams) gave $[\alpha]_D + 145^\circ$ .			
Fraction (I)	from methyl alcohol	(3.0 grams), m. p. 134-136°, had $[\alpha]_D + 151^\circ$	
" (II)	" "	(0.54 gram), m. p. 130-134°, "	$[\alpha]_D + 174^\circ$
" (III)	" "	(0.2 gram), m. p. 177-181°, "	$[\alpha]_D + 226^\circ$
" (IV)	" "	(0.05 gram), m. p. 173-178°, "	$[\alpha]_D + 205^\circ$

Recrystallisation of fraction I did not alter its rotatory power to any appreciable extent. The recrystallised product had  $[\alpha]_D + 150^\circ$ , and melted at 137-138°. Recrystallisation of this specimen gave a product with  $[\alpha]_D + 149^\circ$  and melting point 137-138°. Recrystallisation of fraction II showed it to be composite. When dissolved in boiling methyl alcohol and the solution allowed to cool, about 0.35 gram of crystals separated. These had  $[\alpha]_D + 155^\circ$ , and melted at 137-139°, the substance evidently being identical with that constituting fraction I. The mother liquors from this recrystallisation yielded a small quantity of crystals melting at 165-172°. These are without doubt identical with the substance of high rotatory power constituting fractions III and IV.

The result of the examination of the above product is to show that a definite substance (m. p. 137-138°,  $[\alpha]_D + 150^\circ$ ) is produced in the reaction, in a yield representing about 50 per cent. of that theoretically possible. It is probable that this is either *d*-camphorylidene-methyl-*d*-(or *l*)amino- $\beta$ -gnoscopine, but unfortunately no

\* This had  $[\alpha]_D + 192^\circ$ .

means has yet been found of obtaining the free amino-compound from it.

On analysis, the substance melting at 137—138° gave results too low in carbon when copper oxide was used in the combustion tube. When lead chromate was substituted the following result was obtained:

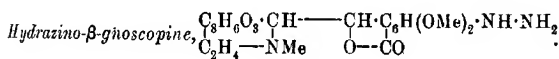
0.1275 gave 0.3120 CO<sub>2</sub> and 0.0770 H<sub>2</sub>O. C=66.7; H=6.7.

C<sub>33</sub>H<sub>38</sub>O<sub>8</sub>N<sub>2</sub> requires C=67.1; H=6.4 per cent.

The suggestion that the above substance is *d*-camphorylidene-methyl-*d*-(or *l*)amino- $\beta$ -gnoscopine is somewhat difficult to reconcile with the facts that the specific rotatory power of the crude product is only +146°, and that the only other substance isolated from the solution (and that only in small amount) had a specific rotation of +206°.

*d*-Camphorylidene-methylamino- $\beta$ -gnoscopine dissolves in warm concentrated hydrochloric acid, and, on cooling the solution, yellow crystals separate in tufts. These are apparently the hydrochloride, and when dried on porous porcelain melt at 164—168°. The original substance is regenerated on adding excess of alkali. Prolonged boiling with hydrochloric acid results in a deep red solution, from which nothing is precipitated by alkali.

The condensation product is very readily soluble in chloroform, ethyl acetate, or benzene, even in the cold. It is quite easily soluble in ethyl and methyl alcohols at their boiling points, and crystallises out on cooling. It is only sparingly soluble in ether, and practically insoluble in light petroleum. When treated with bromine in alcoholic solution (Pope and Read, T., 1913, 103, 444) much more bromine was absorbed than was theoretically necessary to give the hydrobromide of the amino-compound and bromoaldehydocamphor, C<sub>8</sub>H<sub>14</sub> $\begin{matrix} \diagup \text{CBr}\cdot\text{CHO} \\ \diagdown \text{CO} \end{matrix}$ . No definite product could be isolated from the reaction, and doubtless complex bromine substitution products were formed.



In this preparation, amino- $\beta$ -gnoscopine (6 grams) is dissolved in concentrated hydrochloric acid (50 c.c.). Solution occurs only on prolonged stirring, because of the formation of a viscid mass of hydrochloride on the surface of the amino-compound. When the main bulk has dissolved, the solution is cooled to 0°, and a solution of sodium nitrite carefully added until a portion of the diluted reaction mixture gives a colour with starch-potassium iodide paper. To the diazonium solution thus prepared, a solution of 20 grams of

hydrated stannous chloride in 40 c.c. of hydrochloric acid is added all at once. After the reaction has proceeded for an hour, 200 c.c. of water are added, and then, with careful cooling, a solution of 120 grams of potassium hydroxide in 120 c.c. of water. The brownish-yellow precipitate thus formed was found to contain very little inorganic matter, and was collected, washed thoroughly with water, and dried over sulphuric acid. Three such experiments gave a total yield of 15.5 grams, or 82 per cent. of the theoretical amount. The crude substance was in reality almost pure, and melted at 197—200°. *Hydrazino-β-gnoscopine* may be crystallised from alcohol or ethyl acetate, but best from a mixture of chloroform and methyl alcohol, when it separates in colourless prisms, melting and decomposing to a red liquid at 202—204°. All its salts are readily soluble in water:

0.1446 gave 0.3171  $\text{CO}_2$  and 0.0765  $\text{H}_2\text{O}$ .  $\text{C}=59.8$ ;  $\text{H}=5.8$ .

$\text{C}_{22}\text{H}_{25}\text{O}_7\text{N}_3$  requires  $\text{C}=59.6$ ;  $\text{H}=5.6$  per cent.

*Benzylidenehydrazino-β-gnoscopine.*

When hydrazino-β-gnoscopine (2 grams) is boiled for five minutes with benzaldehyde (2 grams) and alcohol (10 c.c.), crystals separate even in the hot liquid, and precipitate almost quantitatively on cooling. The product may be recrystallised from alcohol, in which it is very sparingly soluble. The almost colourless prisms thus obtained melt at 216—218° to a red liquid.

*isopropylidenehydrazino-β-gnoscopine*,  $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$ .

Hydrazino-β-gnoscopine dissolves readily in hot acetone, but after boiling for a few minutes, crystals of the above compound begin to separate, and this separation is soon quantitative. The product crystallises well from a mixture of chloroform and methyl alcohol, and melts at 188—190°:

0.1542 gave 0.3510  $\text{CO}_2$  and 0.0837  $\text{H}_2\text{O}$ .  $\text{C}=62.1$ ;  $\text{H}=6.0$ .

$\text{C}_{25}\text{H}_{26}\text{O}_7\text{N}_3$  requires  $\text{C}=62.1$ ;  $\text{H}=6.0$  per cent.

*l-Menthylidenehydrazino-β-gnoscopine*,  $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}\cdot\text{NH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_{15}$ .

Hydrazino-β-gnoscopine and *l*-menthone when mixed alone or in chloroform solution do not appear to combine, but they do so readily in dilute acetic acid solution. In an actual experiment 8.8 grams of the hydrazine, 3.3 grams of *l*-menthone, 15 c.c. of acetic acid, and 15 c.c. of water were mixed and heated on a steam bath. The hydrazone separated immediately, and in this way a 66 per cent. yield of the almost pure compound was obtained. It was collected, and washed with water and methyl alcohol. The

melting point of the product before recrystallisation was 220–221°. It is readily soluble in chloroform, but crystallises from a mixture of chloroform and methyl alcohol, the melting point of the recrystallised material being still 220–221°.

0.1332 gave 0.3373 CO<sub>2</sub> and 0.0884 H<sub>2</sub>O. C=66.7; H=7.1.

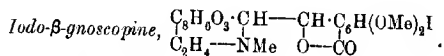
C<sub>22</sub>H<sub>21</sub>O<sub>7</sub>N<sub>3</sub> requires C=66.3; H=7.0 per cent.

A solution of 1.26 grams in 20 c.c. of chloroform gave [α]<sub>D</sub> –51.1°. The following table shows the effect of recrystallisation on the substance:

Taken.	Obtained.	M. p.	[α] <sub>D</sub> <sup>20</sup>
7.5 grams	5.05 grams	220–221°	–48.6°
4.0 "	3.2 "	220–221°	–43.1°
3.0 "	2.4 "	220–221°	–42.5°
1.3 "	0.7 "	220–221°	–38.4°

It would appear from the values of [α]<sub>D</sub> that the hydrazone can be resolved into two constituents by continued crystallisation, but to isolate pure specimens of these, much larger quantities of material than those in our possession would be necessary. The fact that the melting point remains unchanged in the recrystallisation is probably due to its being a decomposition point rather than a true melting point.

The hydrazone is unchanged by hot aqueous solutions of sodium carbonate and sodium hydroxide, and is also recovered unchanged from alcoholic potassium hydroxide solution. It dissolves in cold dilute hydrochloric acid and in warm dilute acetic acid, being reprecipitated by ammonia.



In preparing this substance, amino-β-gnoscopine (3 grams) is dissolved in concentrated hydrochloric acid (30 c.c.), and the solution diazotised in the usual way. The solution of the diazonium salt is then poured into water (100 c.c.), and the diluted solution mixed at once with a solution of 20 grams of potassium iodide in 150 c.c. of water. About ten minutes are allowed for the formation of the iodo-compound, and then sulphur dioxide is passed into the mixture to remove iodine. The crystalline precipitate (which is pale yellow when the operation is successful) is collected and recrystallised from alcohol, when it separates in colourless prisms melting at 185°:

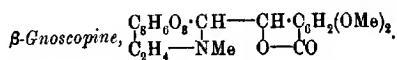
0.1247 gave 0.2250 CO<sub>2</sub> and 0.0486 H<sub>2</sub>O. C=49.2; H=4.3.

0.1120 " 0.0484 AgI. I=23.4.

C<sub>22</sub>H<sub>22</sub>O<sub>7</sub>NI requires C=49.0; H=4.1; I=23.6 per cent.

*Iodo-β-gnoscopine* dissolves readily in dilute acids, and is stable

towards boiling glacial acetic acid. If dissolved in concentrated nitric acid, iodine separates in the free state after some time. If its solution in methyl ethyl ketone is treated with picric acid dissolved in the same solvent, the *picrate* of the base crystallises in bright yellow pyramids, melting at 189—190°. Attempts to prepare an idonarcaine were unsuccessful.



This stereoisomeride of gnoscopine has been obtained by two processes.

#### I. Oxidation of Hydrazino- $\beta$ -gnoscopine.

As the outcome of many trials, the following method was ultimately adopted. The crude hydrazino- $\beta$ -gnoscopine was employed, since considerable loss accrued in its recrystallisation. The best results were, moreover, obtained by working with small quantities. The hydrazine (2.5 grams) is dissolved in a mixture of 8 c.c. of acetic acid and 50 c.c. of water, and then treated in the cold with 60 c.c. of a saturated solution of copper acetate. Evolution of nitrogen soon begins, and the reaction is allowed to proceed until no more is evolved. Cuprous oxide is precipitated, and settles out on the sides of the vessel. The liquid from two such experiments is then poured into a large separating funnel containing about 2 litres of ether; excess of ammonia is added, and the whole shaken vigorously for some time. The ethereal solution is dried and the ether distilled, the residue being crystallised from methyl alcohol. In this way 2.75 grams of the base (m. p. 175—177°) were obtained. This is a 60 per cent. yield calculated on the assumption that the starting material was the pure hydrazine. Actually, therefore, the yield must be greater. A second crystallisation from methyl alcohol raised the melting point to 179—180°, and after three more crystallisations from methyl alcohol, ethyl acetate, and ethyl alcohol, the melting point was raised to 180°, after which further crystallisation did not have any effect.

In an experiment using 2.7 grams of the pure recrystallised hydrazine a total of 1.8 grams of pure  $\beta$ -gnoscopine were obtained, that is, 72 per cent. of the theoretical amount.

The crystals are colourless, rectangular prisms, like miniature planks, and the characteristic pointed ends of crystals of  $\alpha$ -gnoscopine are absent. The melting point (180°) of a specimen of  $\beta$ -gnoscopine was depressed to the neighbourhood of 170° when mixed with  $\alpha$ -gnoscopine:

0.1347 gave 0.3138  $\text{CO}_2$  and 0.0656  $\text{H}_2\text{O}$ .  $\text{C}=63.5$ ;  $\text{H}=5.4$ .

$\text{C}_{22}\text{H}_{23}\text{O}_7\text{N}$  requires  $\text{C}=63.9$ ;  $\text{H}=5.5$  per cent.

## II. Reduction of Iodo- $\beta$ -gnoscopine.

Iodo- $\beta$ -gnoscopine (1.5 grams) is dissolved in boiling methyl alcohol (75 c.c.) and the solution heated on the steam-bath for half an hour with aluminium amalgam obtained by steeping 5 grams of thin aluminium foil in 2 per cent. mercuric chloride solution. The hot liquid is filtered from the aluminium hydroxide, but as this operation cannot be performed quickly enough to avoid crystallisation of a portion of the product, the residue is again boiled with fresh methyl alcohol and again filtered. The combined extracts are concentrated, and the crystals which separate on cooling collected. The yield of the product is practically that demanded by theory. After two or three crystallisations, as in the preparation described above, the product melts at  $180^\circ$ . It melts also at the same temperature when mixed with a specimen of  $\beta$ -gnoscopine obtained from hydrazino- $\beta$ -gnoscopine.

$\beta$ -Gnoscopine forms a sparingly soluble *hydrochloride*, which crystallises in small, colourless, glistening prisms. This is moderately soluble in concentrated hydrochloric acid, and is therefore obtained in only small yield by dissolving  $\beta$ -gnoscopine in the latter. It is best prepared by passing gaseous hydrogen chloride into a solution of  $\beta$ -gnoscopine in glacial acetic acid. When prepared by either of these methods the substance melts at  $86-88^\circ$ , but after remaining overnight in an exhausted desiccator over sulphuric acid it melts at  $224-226^\circ$ , solvent of crystallisation apparently having been abstracted.  $\alpha$ -Gnoscopine has also been observed to form a hydrochloride under similar conditions, but this salt is more soluble, both in concentrated hydrochloric acid and in acetic acid. The hydrochloride of  $\alpha$ -gnoscopine melts at  $238-241^\circ$ .

$\beta$ -Gnoscopine differs, however, from  $\alpha$ -gnoscopine in forming a sparingly soluble *nitrate*. This salt quickly crystallises in microscopic prisms from the solution of the base in dilute nitric acid. The double salts of  $\beta$ -gnoscopine hydrochloride with gold, platinum, and mercuric chlorides resemble in most respects the corresponding narcotine and  $\alpha$ -gnoscopine derivatives.

The *picrate* of  $\beta$ -gnoscopine is readily formed by the addition of an aqueous solution of picric acid to an aqueous solution of  $\beta$ -gnoscopine hydrochloride. It separates as a bright yellow solid, sparingly soluble in water, and it may be crystallised from ethyl or methyl alcohol, from which it separates in short, stout prisms, melting at  $199-201^\circ$ , and decomposing with effervescence at that temperature. The picrate melts under boiling water, and is very



readily soluble in acetone or methyl ethyl ketone. The freshly crystallised substance always seems to contain some solvent of crystallisation.

$\beta$ -Gnoscopine is insoluble in aqueous potassium hydroxide, but on being warmed with an alcoholic solution of the latter, is dissolved, and is not reprecipitated by the addition of water. After the addition of hydrochloric acid, the base is then precipitable by ammonia, the lactone ring evidently having been regenerated.

$\beta$ -Gnoscopine combines readily with methyl sulphate, forming a colourless, viscid mass. This was converted into narceine by the following process. The methosulphate was dissolved in hot water, and enough potassium hydroxide added to render the solution alkaline. After boiling for ten minutes the solution was acidified with acetic acid. On cooling, woolly needles of narceine separated. These, after recrystallisation from water, melted at  $178^{\circ}$ , and the melting point was not depressed when the substance was mixed with a purified specimen of narceine extracted from opium. The above method of obtaining narceine may be conveniently applied as a test-tube reaction for narcotine and  $\alpha$ - and  $\beta$ -gnoscopines.

#### *Oxidation of $\beta$ -Gnoscopine to Cotarnine and Opianic Acid.*

This oxidation was effected by means of dilute nitric acid, but it was found that  $\beta$ -gnoscopine was more resistant to oxidation than either narcotine or  $\alpha$ -gnoscopine.  $\beta$ -Gnoscopine (2 grams) was dissolved in dilute nitric acid (prepared by mixing 10 c.c. of water with 4 c.c. of ordinary concentrated nitric acid), and the solution, which soon deposited crystals of the nitrate, was warmed on the steam-bath until a specimen no longer gave a precipitate with ammonia. The formation of teropiammon which is always observed in the oxidation of narcotine was not observed here. The orange solution was treated with excess of potassium hydroxide, and the precipitated cotarnine collected and identified by conversion into the benzoyl derivative, melting at  $122^{\circ}$ .

The filtrate from the cotarnine was acidified with hydrochloric acid, saturated with ammonium sulphate, and repeatedly extracted with ether. The ethereal solution, after being washed, dried, and evaporated, gave a small quantity of crystalline material, which was identified as opianic acid by means of the characteristic red colour obtained on treatment with xylene and sulphuric acid. The substance also gave an odour of veratraldehyde on heating. Insufficient material was obtained for recrystallisation, and it is probable that much of the opianic acid was further oxidised to hemipinic acid under the above conditions.

*Conversion of  $\beta$ -Gnoscopine into  $\alpha$ -Gnoscopine.*

$\beta$ -Gnoscopine was unchanged by boiling with dilute hydrochloric acid for two hours, but a partial change to  $\alpha$ -gnoscopine took place under the following conditions.  $\beta$ -Gnoscopine (2 grams) was mixed with ethyl alcohol (40 c.c.) and water (10 c.c.), and the mixture heated at  $100^{\circ}$  in sealed tubes for two weeks. The tubes were heated during the working day only, and each morning the major portion of the alkaloid appeared to have crystallised in large prisms. (Complete solution took place at  $100^{\circ}$ .) A slight amount of decomposition occurred, as indicated by the pale orange tinge which the solution acquired. When the tubes were opened, the liquid was drained from the crystals (1.2 grams), which were found to consist of unchanged  $\beta$ -gnoscopine melting at  $179^{\circ}$ . On being diluted with water, the mother liquors deposited a further crop of crystals, which proved to be almost pure  $\alpha$ -gnoscopine melting at  $230$ – $232^{\circ}$ . When mixed with a specimen of pure  $\alpha$ -gnoscopine, the melting point was unchanged.

*Conversion of  $\beta$ -Gnoscopine into Nornarceine.*

When  $\beta$ -gnoscopine is heated with dilute acetic acid for three days at  $105$ – $110^{\circ}$ , it is partly converted into nornarceine. The conversion was carried out according to the method described for  $\alpha$ -gnoscopine by Rabe (*Ber.*, 1907, **40**, 3280), 5.3 grams of  $\beta$ -gnoscopine being heated for seventy hours with a mixture of 9 grams of acetic acid and 50 grams of water. The products were isolated as described by Rabe (*loc. cit.*), the yield of nornarceine being about 0.07 gram. This product showed the characteristic properties of nornarceine. When crystallised from water it melted at  $146^{\circ}$ . It dissolved in alcohol, but quickly separated out again as an anhydrous modification, melting at  $228^{\circ}$ . The remainder of the product proved to be unchanged  $\beta$ -gnoscopine (m. p.  $178$ – $180^{\circ}$ ), no trace of  $\alpha$ -gnoscopine being observed. Further, no meconine was found, as is the case in the similar conversion of narcotine to nornarceine.

The *hydrobromide* of nornarceine was prepared in order to compare it with the product of bromination of nornarceine (p. 2102). It readily separates when nornarceine is dissolved in dilute hydrobromic acid, and consists of very small needles. When first prepared it melts below  $100^{\circ}$ , effervescing about  $115^{\circ}$ . On keeping overnight in an exhausted desiccator over sulphuric acid, it melts at  $128$ – $131^{\circ}$ , some water of crystallisation evidently having been abstracted. When the substance is heated at  $100$ – $105^{\circ}$  in order to drive off the water of crystallisation, it becomes viscid on the

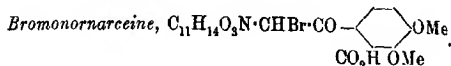
surface, but after cooling can easily be powdered. The salt melts indefinitely between 143° and 152°.

A specimen which had been allowed to dry in the air, and melted at 100—105°, was analysed:

0.1185 gave 0.0410 AgBr. Br=14.7.

$C_{25}H_{25}O_8N \cdot HBr \cdot H_2O$  requires Br=15.1 per cent.

$C_{22}H_{22}O_8N \cdot HBr \cdot 2H_2O$  " Br=14.6 " "



In considering methods for the transformation of  $\beta$ - into  $\alpha$ -nornarceine it was thought possible that if *N*-bromonornarceine could be prepared, elimination of hydrogen bromide from this might give the desired result. Experiments were therefore instituted with the view of preparing this compound, but it was soon discovered that sodium hypobromite reacts with nornarceine in acid solution to give a hydrobromide of bromonornarceine, the bromine being attached to carbon. In alkaline solution the amount of interaction is insignificant, only very small quantities of a halogen-containing compound being produced.

In the preparation of bromonornarceine, the following method was used. Nornarceine (6.8 grams) was dissolved in *N*-hydrochloric acid (150 c.c.) and 29 c.c. of a solution of sodium hypobromite (prepared by adding 2.4 grams of bromine to a solution of 1.8 grams of sodium hydroxide in 29 c.c. of water) were gradually run in. On keeping overnight, crystals were deposited from the acid liquid, the total yield of dry substance being 6.8 grams. The crystals, which were observed under the microscope to consist of large prisms, melted and decomposed at 124—126°. On recrystallisation from water, the melting point is ultimately raised to 132—134°. On heating for two or three hours at 110° this substance apparently partly loses hydrogen bromide, and an attempt to crystallise the heated substance from water reveals a new, much more sparingly soluble compound, which is bromonornarceine. The free base is most easily prepared by treating the aqueous solution of the hydrobromide with sodium carbonate solution. *Bromonornarceine* is readily purified by recrystallisation from water. It melts at 198—200°, effervescing violently. Under the microscope it appears as very minute prisms. It is insoluble in sodium carbonate solution, but readily soluble in dilute sodium hydroxide, being reprecipitated by carbon dioxide:

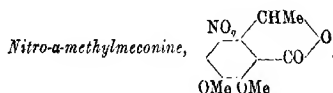
0.1400 gave 0.0493 AgBr. Br=14.9.

$C_{22}H_{24}O_8NBr$  requires Br=15.6 per cent.

The substance dissolves readily in dilute hydrobromic acid, and the hydrobromide separates in prisms melting at  $134-136^{\circ}$ . When mixed with the original product of the bromination (m. p.  $132-134^{\circ}$ ) the melting point was unaltered. The *hydrochloride* is likewise produced by dissolving bromonornarceine in hydrochloric acid, but this salt crystallises from water quite differently from the hydrobromide. The pure salt melts at  $126-128^{\circ}$ .

On treating nornarceine with sodium hypobromite in alkaline solution a small quantity of crystals separated, but these were evidently impure, and contained only about 4 per cent. of bromine. On acidifying the solution, a further small quantity of a substance containing bromine was obtained, but the amount was so small that no further investigation was made, particularly in view of the subsequently discovered fact that  $\beta$ -gnoscopine gives only a very small yield of nornarceine (p. 2101).

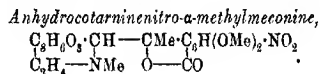
As already mentioned in the introduction, efforts to resolve  $\beta$ -gnoscopine have so far proved unavailing. The  $\alpha$ -bromocamphor-sulphonate showed no tendency to crystallise. Attempts were made also to prepare double salts of  $\beta$ -gnoscopine and morphine with sulphuric and sulphosalicylic acids, but, although no resolution has yet been effected in these cases the investigation will be continued as soon as sufficient  $\beta$ -gnoscopine has been accumulated.



In the preparation of this compound,  $\alpha$ -methylmeconine (4.5 grams), prepared by the action of magnesium methyl iodide on opianic acid (Simonis, Marben, and Merinod, *Ber.*, 1905, **38**, 3981), is treated with 25 c.c. of concentrated nitric acid in the cold for half an hour. The precipitate obtained on the addition of water is collected and crystallised from methyl alcohol. This compound consists of pale yellow leaflets melting at  $110^{\circ}$ , and is much more soluble in ethyl and methyl alcohols than is nitromeconine:

0.1333 gave 0.2567  $\text{CO}_2$  and 0.0543  $\text{H}_2\text{O}$ .  $\text{C} = 52.5$ ;  $\text{H} = 4.5$ .

$\text{C}_{11}\text{H}_{11}\text{O}_6\text{N}$  requires  $\text{C} = 52.2$ ;  $\text{H} = 4.3$  per cent.



In this preparation, nitro- $\alpha$ -methylmeconine (6 grams) and cotarnine (8 grams) were boiled together in 50 c.c. of methyl alcohol for twenty minutes. Crystallisation of the bright yellow condensation

product commenced while the solution was hot. After the solution had cooled, the crystals were collected. As they were obviously mixed with unchanged nitro-compound they were treated with dilute hydrochloric acid, and the solution was filtered and treated with ammonia. The precipitate of the purified condensation product was crystallised from ethyl alcohol, from which it separated in yellow needles, melting and decomposing at  $160^{\circ}$ :

0.1075 gave 0.2327  $\text{CO}_2$  and 0.0506  $\text{H}_2\text{O}$ .  $\text{C}=59.0$ ;  $\text{H}=5.2$ .

$\text{C}_{23}\text{H}_{24}\text{O}_9\text{N}_2$  requires  $\text{C}=58.5$ ;  $\text{H}=5.1$  per cent.

The substance is very similar in its reactions to nitro- $\beta$ -gnoscopine. It is more soluble in organic solvents, but is still very sparingly soluble in methyl alcohol. The base forms salts resembling those of nitro- $\beta$ -gnoscopine, and when its solution in acetic acid is boiled, decomposition to cotarnine and nitromethylmeconine occurs. When reduced in the manner described under the preparation of amino- $\beta$ -gnoscopine, it yields a colourless, crystalline base, which is readily diazotisable. The diazonium salt couples with alkaline  $\beta$ -naphthol, giving an intense crimson azo-compound.

The authors desire to thank the Research Fund Committee of the Chemical Society for a grant,\* which has defrayed a part of the expense of this investigation.

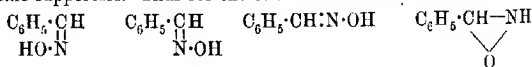
THE UNIVERSITY,  
MANCHESTER.

THE UNIVERSITY,  
SYDNEY.

CXCV.—*The Isomerism of the Oximes. Part IV.  
The Constitution of the N-Methyl Ethers of the  
Aldoximes and the Absorption Spectra of Oximes,  
their Sodium Salts, and Methyl Ethers.*

By OSCAR LISLE BRADY.

WHILST the Hantzsch-Werner stereochemical hypothesis is generally accepted as providing the most satisfactory explanation of the isomerism of the oximes, the earlier theory of Beckmann still finds some supporters. Thus for the two benzaldoximes we have:

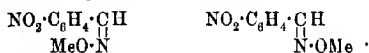


Hantzsch and Werner.

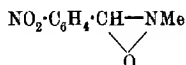
Beckmann.

\* I desire to thank the Research Fund Committee of the Chemical Society for a grant which enabled me to contribute a share towards the expense of a former investigation on the synthesis of narcotine (Perkin and Robinson, T., 1911, 99, 776).  
—R. R.

The existence of two isomeric methyl ethers of, for example, *p*-nitrobenzaloxime, both of which have the methyl group attached to oxygen, cannot be explained by Beckmann's formula but is readily accounted for by that of Hantzsch:



On the other hand, a third methyl ether is known, in which the methyl group is attached directly to nitrogen. Here the stereochemical theory is at fault, and the *iso*-oxime structure of Beckmann



has been generally assigned to this substance.

Forster and Holmes (T., 1908, **93**, 244), from a study of the properties of *isonitrosocamphor* methyl ether, arrived at the conclusion that this substance should be represented by formula I rather than by the more usual structure (II):



Angeli, Alessandri, and Aiazzi-Mancini (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 546) have extended this idea to the *N*-phenyl ethers of the oximes and they regard these compounds as containing a quinquivalent nitrogen atom, thus:  $\text{R} \cdot \text{CH} \cdot \text{NPh} \cdot \text{O}$ . Their conclusions are based on the fact that the *N*-ethers are unstable towards permanganate, differing in this respect from the oxides  $\text{R} \cdot \text{CH} \cdot \text{CH} \cdot \text{R}$ ; further, the action of magnesium phenyl bromide on

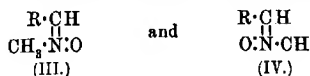


*N*-phenylbenzaloxime, giving  $\beta$ -phenyl- $\beta$ -diphenylmethylhydroxylamine,  $\text{CHPh}_2 \cdot \text{NPh} \cdot \text{OH}$ , is analogous to the action of that compound on benzylideneaniline, giving diphenylanilinomethane,  $\text{CHPh}_2 \cdot \text{NHPh}$ ; in addition, Scheiber (*Ber.*, 1911, **44**, 761) has failed to obtain optically active modifications of *N*-alkylated ald-oximes such as are called for by the *iso*-oxime structure. It would appear that the formula containing quinquivalent nitrogen more easily explains the behaviour of these compounds, especially as they exhibit many unusual properties. The *N*-alkyl ethers of the aromatic ald-oximes are hydrolysed with extraordinary ease; indeed, the *N*-methyl ether of *m*-nitrobenzaloxime is at once hydrolysed by cold concentrated hydrochloric acid; moreover, these compounds readily form additive products with sodium iodide (Goldschmidt

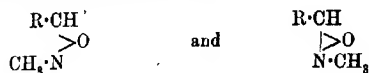
and Kjellin, *Ber.*, 1891, **24**, 2812), calcium chloride, phenyl carbimide, and hydrogen haloids.

Before accepting the new structure, however, there are several facts to be noted which do not seem to have been fully considered by previous investigators.

A structure involving a quinquivalent nitrogen atom allows for the existence of two isomeric nitrogen ethers, namely:



as does also the *iso*-oxime structure:

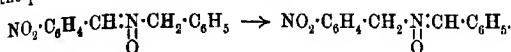


although here the isomerism depends only on the relative position of the hydrogen atom and the methyl group.

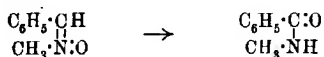
Luxmoore (T., 1896, **69**, 183) describes a second *N*-methyl ether of benzaldoxime, but Scheiber (*Annalen*, 1909, **356**, 215) has shown that the second ether obtained by Luxmoore is probably a hydrated form of the first, the same reason being assigned for the discrepancy in the melting point, etc., of *N*-methylanisalaldoxime as prepared by Goldschmidt (*Ber.*, 1890, **23**, 2186) and by Beckmann and Netscher. The existence of these hydrates is in accordance with the behaviour of the similarly constituted trimethylamine oxide, which readily forms hydrates and appears to act as  $\text{NMe}_3(\text{OH})_2$ , forming a salt,  $\text{NMe}_3\text{Cl}\cdot\text{OH}$ , with hydrochloric acid (Dunstan and Goulding, T., 1899, **75**, 795). It is noteworthy that the *N*-methyl ether of benzaldoxime is soluble in water and can be extracted from its aqueous solutions only with difficulty. These compounds, however, differ in many respects from the amine oxides; they do not give alkaline solution, indeed, the *N*-ethers of the nitrobenzaldoximes are but very sparingly soluble in water; they are not hygroscopic, and do not form salts with the same ease; thus the *N*-methyl ether of *p*-nitrobenzaldoxime is soluble in 50 per cent. hydrochloric acid in the cold, but the solution soon deposits crystals of *p*-nitrobenzaldehyde owing to hydrolysis; this offers a serious objection to the formula suggested by Angeli and his co-workers.

The only other recorded cases of isomerism among compounds of this class are those of the *N*-benzyl ether of *p*-nitrobenzaldoxime (Behrend and König, *Ber.*, 1890, **23**, 2571) and the *N*-*p*-chlorobenzyl ether of benzaldoxime (Neubauer, *Annalen*, 1897, **298**, 187), both of which exist in two forms, the second being obtained from the first by the action of sodium ethoxide. These are apparently

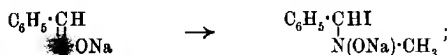
not stereoisomerides, their existence being explained by a change in the position of the double bond, thus:



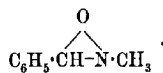
There is little direct evidence of the spacial structure of the *N*-ethers but formula III seems at first sight to be the more probable as these compounds are obtained more easily from the *syn*-oximes, and Beckmann (*Annalen*, 1909, **365**, 208) has shown that *N*-methylbenzaldoxime on treatment with phosphorus pentachloride in ether yields *N*-methylbenzamide, a reaction which may be regarded as a case of the Beckmann change:



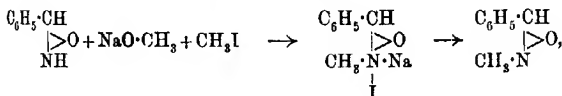
On the other hand, since Beckmann has described the preparation of the *N*-methyl ethers of such compounds as the hydroxybenzaldoximes from the hydroxybenzaldehydes and  $\beta$ -methylhydroxylamine, it seems more reasonable, as the hydroxybenzaldoximes are known only in the *anti*-form (compare Brady and Dunn, this vol., p. 824), to assign an *anti*- rather than a *syn*-structure to these compounds. The mechanism of the formation of the *N*-methyl ethers has received several interpretations; Goldschmidt (*loc. cit.*) explains the formation of the sodium iodide additive product as follows:



this compound then loses sodium iodide to give the *N*-ether,



Luxmoore (*loc. cit.*) assumes that the addition takes place at the nitrogen atom, which becomes quinquivalent:



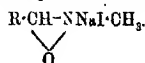
In this way a *N*-methyl ether is obtained from the *syn*-sodium salt, in which the hydrogen atom and the methyl group are in the *anti*-position to one another. Luxmoore, however, has had to assume that the sodium salt of the *syn*-aldoxime has the Beckmann *iso*-oxime structure, and also that the two hydrogen atoms are in a *syn*-position to one another, in fact, he combines the stereochemical and



*iso*-oxime structures. This interpretation does not seem feasible

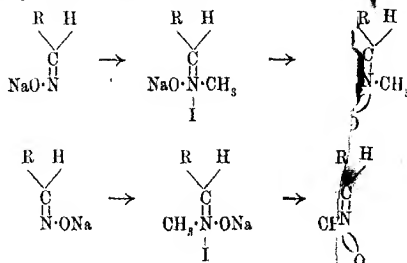
and in addition a compound of the structure  $\text{R}-\text{CH}-\text{N}^{\cdot}\cdot\text{CH}_3$  would

not be likely to form additive compounds with sodium iodide or calcium chloride so readily if it is supposed that in the formation of these compounds the nitrogen atom becomes quinquivalent, thus:

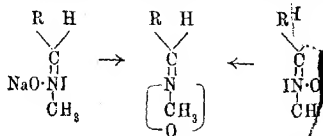


There remains to be considered the possibility that the *N*-ethers themselves contain quinquivalent nitrogen.

If the addition of the elements of methyl iodide takes place at the nitrogen atom, the structure of the products will depend on the relative positions taken by the methyl group and the iodine atom; if the latter is attached at the valency direction in the same plane as the double bonds, an *anti*- and a *syn-N*-ether will be obtained according as to which isomeride is employed:

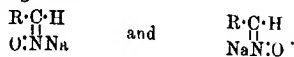


If, on the other hand, the methyl group takes this position there will be no chance of *anti-syn*-isomerism in the product:

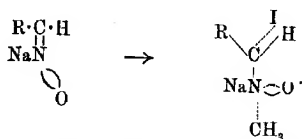


On this supposition the fact that the sodium salt of the *syn*-oxime yields a much larger quantity of the *N*-ether than that of the *anti*-oxime can perhaps be explained by the iodine taking up a position near the aromatic nucleus in the case of the *anti*-derivative whilst in the case of the *syn*-compound, this position being occupied by the stable *O*-methyl ether is formed. A tempting explanation of the

action of methyl iodide on the sodium salts of the oximes is afforded if it be considered that the sodium salts of the oximes are capable of reacting in the forms:

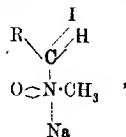


Methyl iodide might act on this compound in two ways, addition taking place either at the carbon-nitrogen or at the oxygen-nitrogen double bond. In the former case the reaction may be represented thus:

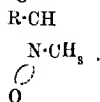


The dotted valency directions indicate that these are at right angles to the plane of the paper.

If rotation takes place through one right angle to bring the iodine and oxygen atoms together, the compound becomes

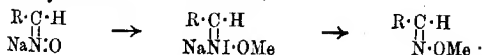


which loses sodium iodide to give:



In this way the *anti*-form of the *N*-methyl ether is obtained from the sodium salt of the *syn*-oxime; conversely, the *anti*-sodium salt would yield the *syn-N*-methyl ether.

If the addition takes place at the oxygen-nitrogen double bond *O*-methyl ethers will be obtained:



If both these actions can take place on treating the sodium salt of the *syn*-oxime with methyl iodide, it is to be expected that the reaction will take place in such a way as to yield the most stable product, that is, the *anti-N*-methyl ether, although a little of the stable *syn-O*-methyl ether will be obtained. On the other hand, sodium salt of the *anti*-oxime will give mainly the stable *anti-O*-

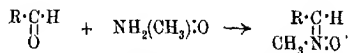
methyl ether and very little of the *syn-N*-methyl ether. This is what is found actually to be the case, with the exception that the *N*-ethers obtained are identical, but this may be explained by the extreme instability of the *syn*-ethers, the additive compound formed by the addition of the methyl group and iodine at the double bond between carbon and nitrogen undergoing intramolecular change leading to the formation of the *anti-N*-ether.

It is possible that the silver salts of the oximes which, with methyl iodide, give *O*-ethers unmixed with *N*-ether may have the normal structure, although a constitution similar to that of the sodium salts still affords an explanation of their action. Here the addition takes place solely at the nitrogen-oxygen double bond to ensure the more easy elimination of silver iodide.

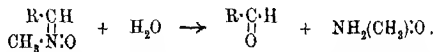
If this explanation is to be accepted, however, it must be noted that the sodium iodide additive compound of *N*-methylbenzaldoxime has a different structure from that assigned to it in the earlier portion of this paper; it is, however, possible that the sodium iodide additive compound isolated in the preparation of the *N*-ethers, or by evaporating a solution of the *N*-ether with sodium iodide, is not the primary product of the action of methyl iodide on the sodium salt of the *syn*-oxime, but a secondary product formed from the *N*-ether and the sodium iodide produced by the reaction.

The view that the sodium salts of the oximes can exist in a tautomeric form with the alkali metal attached directly to nitrogen in preference to oxygen is not without analogy, for there is little doubt that the alkali cyanates should be represented as isocyanates,  $\text{NaN}^+\text{C}^-\text{O}$ , rather than by the cyanate structure  $\text{NaO}^-\text{C}^+\text{N}$ .

The formation of the *N*-methyl ethers of the aromatic aldioximes from the aldehyde and  $\beta$ -*N*-methylhydroxylamine (Beckmann, *loc. cit.*) can be explained if that compound is regarded as acting in its tautomeric form,  $\text{NH}_2(\text{CH}_3)\text{O}$ , of which the amine oxides are derivatives:



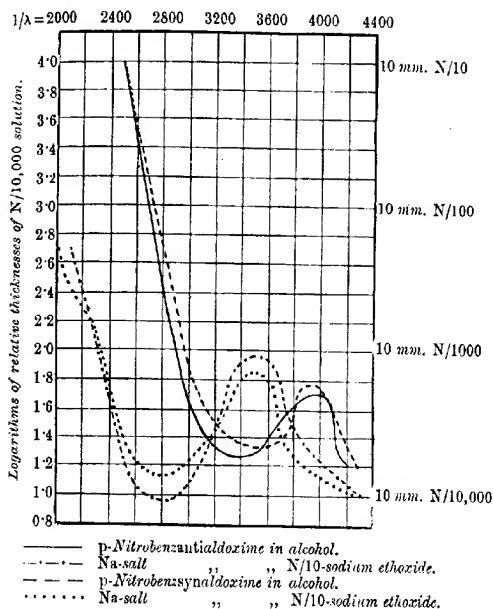
Similarly, the ready hydrolysis of the *N*-ethers may be interpreted thus:



It was thought possible that a study of the absorption spectra of these compounds would throw some light on the question, and the author has accordingly photographed the absorption spectra of benzanti- and benzsyn-aldoxime and the corresponding sodium salts, the *O*-methyl ether of benzantialdoxime and the *N*-methyl ether of benzaldoxime, the two *p*-nitrobenzaldoximes and their sodium salts

and *O*-methyl ethers, and the *N*-methyl ether of *p*-nitrobenzaldehyde. The chief reason for choosing *p*-nitrobenzaldehyde as a substituted benzaldehyde was that the author had a small quantity of the *syn-O*-methyl ether of this compound of undoubted purity (compare Brady and Dunn, T., 1913, 103, 1625), whereas it is questionable whether most of the other *syn-O*-methyl ethers described in the literature are pure, owing to the difficulty of preparing these compounds in large quantities and freeing them from

FIG. 1.



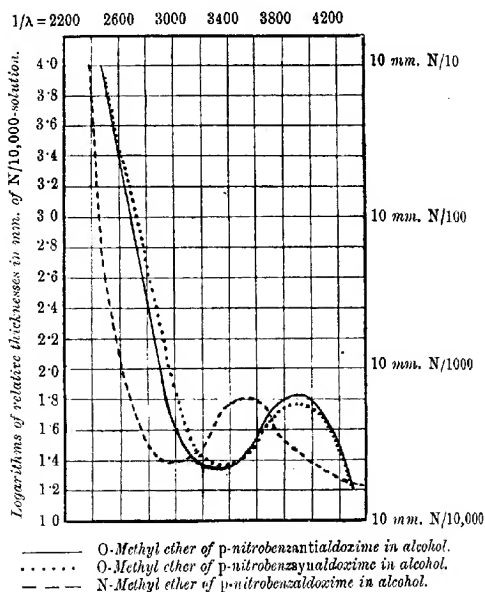
the *anti*-isomeride. The *syn-O*-methyl ether of benzaldehyde has been described, although the characteristic fruity odour observed on treating the sodium salt of benzaldehyde with methyl iodide probably due to the formation of this compound in addition to the *N*-methyl ether (Goldschmidt and Kjellin, *loc. cit.*).

After taking the photographs it was found that Hantzsch (*Ber.*, 1910, 43, 1661) had already published the absorption spectra of the two *p*-nitrobenzaldehydes and their sodium salts in a paper under the title of "Homochromoisomerism." He did not, however,

consider the ethers, and his conclusions were relative to his theory of homochromoisomerism and have no bearing on the question in hand.

The curves obtained by the present author independently are practically identical with those of Hantzsch, although the sodium salts show a rather deeper band. It was found necessary to take the sodium salts in a  $N/10$ -solution of sodium ethoxide and to dilute the solution with  $N/10$ -sodium ethoxide, as, if pure alcohol was used for dilution, the amount of the absorption was increased. Whilst

FIG. 2.



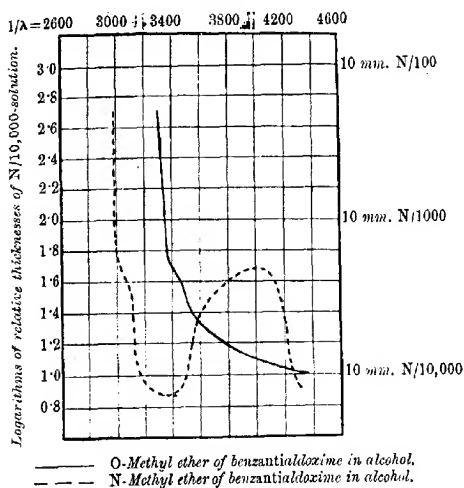
at greater concentrations the absorption of the oximes is identical, with more dilute solutions there is quite a marked difference, the usual rule being followed that the *anti* is more absorptive than the *syn*-isomeride, as is the case with the general absorption exhibited by maleic and fumaric acids.

The sodium salts in dilute solution behave similarly, although in more concentrated solution a reversal takes place, and the *syn*-isomeride is more absorptive than the *anti*. The curves for the sodium salts show a very marked shift in the position of the band

wards the red end of the spectrum, and, whilst the solutions of the oximes are colourless, those of the sodium salts are bright yellow. The curves obtained from the three methyl ethers are shown in fig. 2.

Those of the two *O*-methyl ethers are practically coincident with those of the corresponding oximes; on the other hand, the curve for the *N*-methyl ether shows a shift towards the red end of the spectrum, although not so great as in the case of the sodium salts. A similar result is to be observed in the case of the *O*-methyl ether and *N*-methyl ether of benzaldoxime. Here, however, the effect is

FIG. 3.

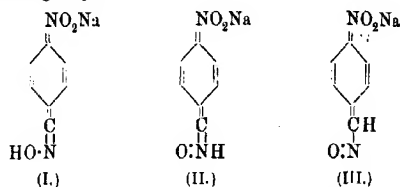


much more marked, and, whilst the *O*-methyl ether exhibits only general absorption, the *N*-ether shows a deep band. The effect of conjugated double bonds in producing colour or increased absorption has long been known, and, whilst it is necessary to observe caution in interpreting spectroscopic results when applied to organic compounds, it seems reasonable to suppose that the spectroscopic evidence is in favour of the structure  $R \cdot CH \cdot N(CH_3) \cdot O$  for the *N*-methyl ethers of the aromatic aldoximes rather than against it (compare Crymble, Stewart, Wright, and Glendinning, T., 1911, 99, 451).

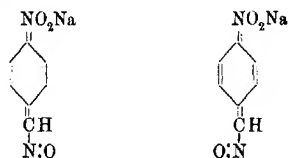
The evidence is also in favour of a structure for the two oximes similar to that of the *O*-methyl ethers, that is, the structure assigned

to these compounds by Hantzsch; moreover, the absorption spectra of the oximes resemble those of *cis-trans*-isomerides.

The character of the absorption spectra of the nitrobenzaldoximes and their sodium salts raises the vexed question of the relation between constitution and colour. Baly, Tuck, and Marsden (T., 1910, 97, 571) have discarded the quinonoid structure proposed by Hantzsch for the sodium salts of the nitrophenols, etc., but this theory still finds many supporters. Now both the *syn*- and *anti*-forms of *p*-nitrobenzaldoxime are practically colourless, whilst their sodium salts are bright yellow. If, as Hantzsch supposes, in the case of the nitrophenols the sodium salt exists in the *aci*-form, the sodium salt of *p*-nitrobenzaldoxime can be written structurally only in the following ways:



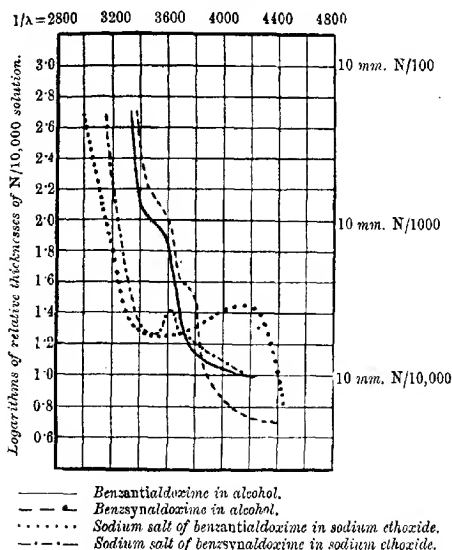
Formula I is very improbable as it is impossible to obtain a disodium salt such as this demands; moreover, the sodium salt of *m*-nitroacetophenoneoxime,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe:NOH}$ , is also yellow, whilst the parent substance is, when pure, colourless. It is to be supposed that the change in this compound on salt-formation would resemble that of the nitrobenzaldoximes, and here there is no opportunity for such a structure as I above. The same reason disposes of formula II. There remains formula III, to which there are also very serious objections: first, the formation of a coloured *N*-methyl ether from the sodium salt of the *syn*-oxime, in which the methyl group is undoubtedly attached to the oximino-nitrogen atom, and secondly, if such a structure is assigned to both *syn*- and *anti*-oxime sodium salts:



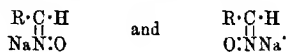
there is free rotation of the nitrogen atom, and these two compounds would be identical. It would, therefore, be expected that, on acidifying a solution of the sodium salts of either oxime, either the

stable *anti*-oxime would be obtained or an equilibrium mixture of the *syn*- and *anti*-oximes. It is well known that on acidifying a solution of the sodium salt of *p*-nitrobenzanti-aldoxime the *anti*-oxime is obtained in a pure state, and the author has found that on acidifying a solution of the sodium salt of *p*-nitrobenzsynaldoxime practically pure *syn*-oxime is recovered, even if the alkaline solution has remained for an hour. In addition, the preparation of the isomeric *O*-methyl ethers of *p*-nitrobenzsyn- and *anti*-aldoxime from the silver salts obtained from the corresponding sodium salts

FIG. 4.



shows that the isomerism persists even in the sodium salts. It is, therefore, evident that the sodium salts of the nitro-oximes do not exist in the *aci*-form. On the other hand, it is not possible to show that there is no change in structure on salt-formation, and it is quite possible that the sodium salts exist in the forms:



Hartley and Dobbie (T., 1900, 77, 509) have stated that the absorption spectra of the two benzaldoximes are identical, and, as



this was not in agreement with the results for the *p*-nitrobenzaloximes, this work has been repeated. It has been found that the *anti*- is slightly more absorptive than the *syn*-isomeride, the benzaldoximes thus forming no exception to the general rule.

In a private communication to the author Dr. Dobbie states that this was observed by himself and the late Prof. Hartley, but, as the difference did not amount to more than a few units, it was not considered at the time of sufficient importance for special attention to be called to it.

There is some difficulty in deciding whether a band exists in the absorption spectra of the benzaldoximes, as Drs. Dobbie and Fox (private communication) by taking a large number of thicknesses between 30 and 15 mm. of *N*/10,000 solution have confirmed the presence of a shallow but decided band in the position originally found by Hartley and Dobbie. The author, however, has taken several photographs of this substance without detecting this band. The benzantialdoxime used by the author was prepared in the usual way, and after pressing on several porous plates to remove oily matter it was recrystallised from benzene and light petroleum.\* The *syn*-oxime was recrystallised from warm benzene, was without odour and melted sharply at 132°. The sodium salts of these compounds exhibit a decided shift towards the red end of the spectrum and show a shallow band. The oximes and their sodium salts show in this respect an analogy to the *O*- and *N*-methyl ethers of benzaldoxime.

In conclusion, the author wishes to express his indebtedness to Dr. Crymble for taking the photographs of the *p*-nitrobenzaloximes and their ethers, and to Miss R. M. Johnson for assistance in taking the other photographs.

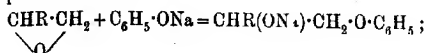
ROYAL COLLEGE OF SCIENCE,  
THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON.

\* The failure of the present author to obtain a band does not seem to be due to a defect in the instrument or to impurity in the oxime. The same solution as was used to photograph the absorption spectrum of the oxime was employed, with the addition of a few drops of sodium ethoxide solution, to photograph that of the sodium salt; in the latter case the band is plainly marked, whereas, if the increased absorption was due to the spectroscop being at fault, or to an impurity being present, it would hardly be expected that light previously cut off by either of these causes would now be transmitted.

CXCVI.—*The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides.*

By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

OBSERVATIONS on the action of epichlorohydrin and of aryl ethers of glycide on alkaline solutions of phenols (Lindeman, *Ber.*, 1891, 24, 2147; Boyd and Marle, *T.*, 1910, 97, 1788) have shown that the olefine oxide group reacts readily with sodium phenoxides to produce phenolic ethers:



and the reaction appeared to us to be one that might with advantage be studied quantitatively with the object of ascertaining how the speed of combination varies with (i) the constitution of the phenol, and (ii) that of the olefine oxide.

The olefine oxides which we have chosen for investigation are ethylene and propylene oxides.

It was observed by Roithner (*Monatsh.*, 1894, 15, 674) that the former combines with phenol when heated with it for some hours at 150°. The reaction, however, proceeds much more rapidly in the presence of an alkali, and can, we find, be conveniently carried out in alcoholic solution at temperatures between 50° and 100°.

*Method of Experiment.*

The following is a brief account of the method which we adopted for carrying out our experiments. Further details will be found in the experimental portion of the paper.

A standard solution of each phenol in 98 per cent. ethyl alcohol was prepared, and a suitable quantity of this was mixed with sodium ethoxide solution and ethyl alcohol in the proportions necessary to produce a liquid normal as regards the amount of phenol and twentieth normal as regards the sodium present. The ethylene or propylene oxide was weighed in a sealed bulb, the amount taken varying in most cases between 0.1 and 0.5 gram. The bulb was placed in a glass tube along with an equivalent quantity of the alkaline phenol solution, and the tube was then sealed at the blowpipe, care being taken to prevent the introduction of any carbon dioxide during the process. In the majority of the experiments the reaction tube was of such a length that the space unoccupied by the reaction liquid was about one and a-half times or twice the volume of the liquid; but it was found that an increase of the air space up to at least three times the volume

of the liquid present had no important influence on the speed of the reaction. After the bulb containing the olefine oxide had been broken, the reaction tube was placed in a thermostat at 70.4° and heated for one hour or longer. It was then quickly cooled and opened, and the contents were transferred to a separating funnel. Ether was added (or in some cases light petroleum), and the ethereal solution was shaken repeatedly with a dilute solution of potassium hydroxide, until the alkaline washings were found to be free from phenol. The series of alkaline liquors was then shaken two or three times with fresh quantities of ether. The combined ethereal solutions were dried over potassium carbonate, and the ether distilled off from a tared flask. The resultant glycol aryl ether was dried for some hours in a vacuum desiccator over sulphuric acid, and then weighed.

Preliminary experiments in which the olefine oxides were heated with  $N/20$  sodium ethoxide solution in the absence of any phenol, and the process otherwise carried out as above indicated, resulted in no weighable quantity of product being obtained on evaporation of the ether.

#### Theory of the Reaction.

Ethylene oxide, as already stated, can combine with phenols in the absence of alkali, but at 70.4° the temperature employed in our experiments, the speed of combination in the case of the less acidic phenols is small in comparison with the speed with which the oxide unites with the sodium phenoxide. This is shown by the following figures obtained in the case of *p*-cresol:

Reaction solution.	Percentage of ethylene oxide converted into glycol <i>p</i> -tolyl ether in 2 hours at 70.4°.
(i) <i>N</i> - <i>p</i> -Cresol .....	1.0
(ii) <i>N</i> - <i>p</i> -Cresol, $N/20$ -Na .....	72.5

The yield of glycol *p*-tolyl ether obtained in the second case is thus due almost entirely to the sodium *p*-tolyl oxide; and since the concentration of the sodium tolyloxide must remain constant so long as a considerable excess of *p*-cresol is present, it follows that the rate of formation of glycol *p*-tolyl ether during the greater part of the reaction-time must be approximately in accordance with the formula for a unimolecular reaction. The following figures illustrate this:

Reaction solution.	Time of heating.	Yield of glycol <i>p</i> -tolyl ether. Per cent.	$k = \frac{1}{t} \log \frac{100}{100-x}$
<i>N</i> - <i>p</i> -Cresol	1 hour	47.0	0.276
$N/20$ -Na	2 hours	71.8	0.275
	2 "	73.2	0.286

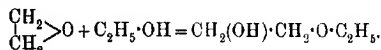
In the case of propylene oxide no weighable quantity of the propylene glycol ether was obtained when propylene oxide was heated with *N-p*-cresol in the absence of alkali for two hours.

In the case of the more acidic phenols the effect of the presence of the free phenol is more important, as the following figures for ethylene oxide and 2:4:6-trichlorophenol show:

Reaction solution.	Time of heating.	Yield of glycol trichlorophenyl ether.		$k = \frac{1}{t} \log \frac{100}{100-x}$ .
		Per cent.		
(i) <i>N</i> -Trichlorophenol ...	2 hours	2.0		—
(ii) <i>N</i> -Trichlorophenol } <i>N</i> /20·Na }	2 „	29.4		0.075
	4 „	48.1		0.071
	4 „	51.2		0.078
Mean				0.075

In this case the velocity-constant calculated for the sodium salt is too high. The corrected constant for sodium trichlorophenoxide, taking into account the effect of the free trichlorophenol, would be approximately 0.071. As this correction, however, does not affect the main results of the investigation, the uncorrected results only are given in the table on p. 2123.

Another factor which affects the values of the observed velocity-constants is the action of the olefine oxide on the alcohol used as a solvent. It is probable that olefine oxides react slowly with ethyl alcohol, and more rapidly with sodium ethoxide, to form glycol ethyl ethers:



Owing, however, to the solubility in water of the products of this reaction in the case of ethylene or propylene oxide, the occurrence of this subsidiary reaction does not prevent the approximate estimation of the yield of glycol aryl ether by the method we have adopted. It has the effect, however, of slightly diminishing the values of the velocity-constants obtained for the sodium phenoxides. The magnitude of the effect so produced can be estimated from a consideration of the speed of combination of the olefine oxide and alcohol, and this can be determined approximately by measuring the maximum yields of glycol aryl ethers obtained in the case of the more acidic phenols, when the solutions remain neutral throughout the whole experiment.

The following data refer to ethylene oxide:

Reaction solution.	Yield in 2 hours. Maximum yield.	
	Per cent.	Per cent.
<i>N-p</i> -Nitrophenol } ...	5.6	74
<i>N</i> /20·Na }		
<i>N-m</i> -Nitrophenol } ...	13.4	87
<i>N</i> /20·Na }		

Since a large excess of alcohol is present during the whole experiment, the reaction between the alcohol and the ethylene oxide may be regarded as a unimolecular one, and hence the ratio of the speeds of the two concurrent reactions, combination with alcohol, and combination with the sodium derivative of *p*-nitrophenol, may be taken as 26/74. Consequently, in the case of the *p*-nitrophenol solution we obtain for the percentage of ethylene oxide lost in two hours by combination with alcohol,  $26/74 \times 5.6 = 2$  approximately. The figures in the case of *m*-nitrophenol give a similar result. Hence in the case of phenols sufficiently reactive for the experiments to be completed in two or four hours it has not been thought necessary to make any correction for this factor.

The yield of glycol aryl ether in two or four hours with some phenols, however, is so small that experiments were made involving longer periods.

In such cases the correction becomes important, as is shown by the following figures:

Time in hours.	Yield. Per cent.	<i>k</i> uncorrected.	<i>k</i> corrected.
<i>N</i> - <i>o</i> -Nitrophenol, <i>N</i> /20- <i>Na</i> *, and ethylene oxide.			
2	3.3	0.0073	0.00736
46	47.5	0.0061	0.00740
<i>N</i> - <i>p</i> -Hydroxybenzonitrile, <i>N</i> /20- <i>Na</i> *, and propylene oxide.			
2	6.69	0.0150	0.0152
11	29.6	0.0138	0.0144
<i>N</i> -Salicylonitrile, <i>N</i> /20- <i>Na</i> *, and propylene oxide.			
2	8.49	0.0193	0.0195
15	45.0	0.0173	0.0192

The formula used for correction of the velocity-constant is as follows:

$$K = \frac{Y}{100} \left( \frac{1}{t} \log \frac{1}{1 - \frac{x}{Y}} \right)^*$$

\* Let *K* = velocity-constant of formation of aryl ether.

„ *K* = „ „ „ „ ethyl ether.

„ *x* = percentage of ethylene oxide transformed into aryl ether in *t* hours.

„ *x*<sup>1</sup> = „ „ „ „ ethyl „ „

„ *Y* = maximum percentage yield of aryl ether.

Then  $x + x^1$  = total percentage of ethylene oxide transformed in *t* hours.

Hence

$$K + K^1 = \frac{1}{t} \log \frac{100}{100 - (x + x^1)}$$

$$\text{But } \frac{x}{x + x^1} = \frac{Y}{100} \quad \therefore x + x^1 = \frac{100x}{Y}$$

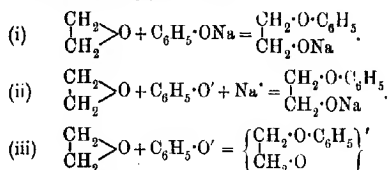
$$\therefore K + K^1 = \frac{1}{t} \log \frac{100}{100 - \frac{100x}{Y}}$$

where  $K$  is the corrected velocity-constant for the reaction between the olefine oxide and the sodium phenoxide,  $x$  is the percentage yield in  $t$  hours, and  $Y$  is the maximum yield per cent.

This formula is based on the assumption that the reactions between the olefine oxide and the alcohol and sodium phenoxide respectively may both be regarded as unimolecular.

With regard to the mechanism of the reaction between the olefine oxide and the sodium phenoxide, three possibilities present themselves.

The reaction may occur (i) between the oxide molecule and the undissociated sodium phenoxide, or (ii) between the oxide molecule and the sodium and phenoxy-ions, or (iii) it may consist in the combination of the oxide molecule with the phenoxy-ion only, a new ion being formed. This would then react with the excess of phenol to give the undissociated glycol ether:



As far as our experiments admit of a conclusion being drawn with regard to this question, it would appear that the third hypothesis is the most probable one. This is shown by the following considerations.

The effect on the velocity of reaction produced by an alteration in the concentration of the sodium phenoxide must evidently be different in the three cases. If, for example, the concentration of the sodium phenoxide were reduced from  $N/20$  to  $N/40$ , then, owing to the increase in the degree of dissociation resulting from the dilution, the active mass of undissociated sodium phenoxide would be reduced to less than one-half of its previous value; hence, assuming equation (i) to represent the mechanism of the reaction, a diminution of the speed of the reaction to less than one-half of its previous value must follow.

$$= \frac{1}{t} \log \frac{1}{1 - \frac{x}{Y}}$$

And

$$\frac{K}{K+K^1} = \frac{Y}{100} \quad \therefore K = \frac{Y}{100(K+K^1)}.$$

$$\therefore K = \frac{Y}{100} \left( \frac{1}{t} \log \frac{1}{1 - \frac{x}{Y}} \right).$$

In the case represented by equation (ii), halving the concentration of the sodium phenoxide would result in a reduction of the speed of the reaction to one-quarter of its former value, supposing the degree of dissociation were unaltered. The increase in the degree of dissociation which accompanies the dilution would prevent the reduction in speed being quite so great, but the total result must be again a diminution in speed to less than one-half. On the other hand, in the case represented by equation (iii) a diminution in the concentration of the sodium phenoxide from  $N/20$  to  $N/40$  would result in a diminution in the speed of the reaction to a value greater than one-half the original one, for the increase in the degree of dissociation will counterbalance, to some extent, the diminution in concentration of the phenolic salt.

Experiments with *p*-cresol and ethylene oxide gave the following results:

Reaction solution.	Time.	Yield. Per cent.	<i>k</i> .	Mean <i>k</i> .
(i) <i>N-p</i> -Cresol $N/20\text{-Na}^+$ } ...	1 hour	47.0	0.276	0.279
	2 hours	71.8	0.275	
	2 "	73.2	0.286	
(ii) <i>N-p</i> -Cresol $N/40\text{-Na}^+$ } ...	2 "	48.9	0.146	0.157
	2 "	52.5	0.162	
	4 "	77.6	0.163	

These facts are in harmony with the view of the reaction represented by equation (iii).

#### *Summary of Results.*

The following table contains the results of experiments carried out at  $70.4^\circ$  with *N*-phenol,  $N/20\text{-Na}^+$  alcoholic solutions. The velocity-constants given are mean values calculated on the results of at least two experiments of different periods of duration. The experimental error varies somewhat with different phenols, but the figures already quoted for *p*-cresol, 2:4:6-trichlorophenol, *o*-nitrophenol, *p*-hydroxybenzonitrile, and salicylonitrile may be taken as typical of the results obtained generally.

In a number of cases two or more experiments of the same period of duration were carried out, and in the column headed "Yield in two hours" the limits obtained in separate experiments of two hours' duration are given, the number of experiments carried out being indicated by the figure in brackets.

No.	Phenol.	Ethylene oxide.			Propylene oxide.		
		Yield in 2 hours. Per cent.	Maximum yield. Per cent.	$k = \frac{1}{t} \log \frac{100}{100-x}$	Yield in 2 hours. Per cent.	Maximum yield. Per cent.	$k = \frac{1}{t} \log \frac{100}{100-x}$
1.	<i>p</i> -Cumenol ...	78.9	94.2	0.338	44.8	89.6	0.125
2.	Thymol .....	74.9	90.7	0.311	39.9—38.5 (3)	90.6	0.107
3.	<i>m</i> -Dimethyl-aminophenol	*	*	*	38.9	92.6	0.105
4.	<i>p</i> -Cresol .....	73.2—71.8 (2)	97.0	0.279	38.5—36.3 (3)	92.5	0.101
5.	Carvacrol ...	68.8	92.9	0.257	38.8	89.8	0.101
6.	<i>m</i> -Cresol .....	69.8—68.1 (2)	98.0	0.256	32.1—31.8	90.9	0.083
7.	<i>p</i> -Xylenol ...	67.8	91.9	0.244	†	88.9	0.092
8.	Eugenol .....	65.6—62.8 (2)	96.0	0.226	32.0	95.8	0.080
9.	<i>o</i> -Cresol .....	64.5—64.1 (2)	94.5	0.225	30.8—28.9 (2)	94.1	0.078
10.	Phenol.....	60.8—60.3 (2)	96.7	0.205	30.1—28.5 (3)	92.7	0.075
11.	<i>o</i> -Naphthol .	64.9	97.5	0.173	30.9	97.9	0.083
12.	Guaiacol ...	53.7	99.3	0.171	26.2	91.6	0.064
13.	<i>p</i> -Naphthol .	48.7—48.3 (2)	95.1	0.144	22.5—21.1	94.2	0.053
14.	<i>p</i> -Chloro-phenol	40.6—38.3 (2)	95.5	0.108	17.7—16.8	92.9	0.042
15.	<i>o</i> -Chloro-phenol	39.0—38.6 (2)	95.9	0.104	21.0—19.7 (2)	96.1	0.050
16.	<i>m</i> -Chloro-phenol	37.5—36.8 (2)	95.7	0.101	17.9	92.0	0.043
17.	2:4:6-Tri-bromophenol	38.6—37.6 (3)	93.9	0.099	26.9—25.8 (3)	90.8	0.065
18.	2:4:6-Tri-chlorophenol	29.4	92.7	0.075	19.4—18.8 (3)	92.2	0.045
19.	<i>p</i> -Benzene-azophenol	20.9	90.7	0.050	10.2	86.0	0.023
20.	<i>m</i> -Hydroxy-benzonitrile	19.1	90.5	0.044	9.99	86.8	0.0224
21.	Salicylonitrile	14.3	81.9	0.033	8.49	79.5	0.0193
22.	<i>m</i> -Nitrophenol	13.4	87.2	0.032	6.73	85.0	0.0152
23.	<i>p</i> -Hydroxy-benzonitrile	11.1	81.6	0.026	6.69	81.4	0.0150
24.	<i>p</i> -Nitrophenol	5.6	73.6	0.013	3.2—3.14 (2)	71.6	0.0075
25.	<i>o</i> -Nitrophenol	3.3	71.1	0.0073	2.38	73.4	0.0035

\* Owing to the solubility in water of glycol *m*-dimethylaminophenyl ether it was not found possible to estimate the yield in the case of ethylene oxide.

† The velocity-constant was calculated from experiments of one, three, and four hours' duration. The percentage yield in three hours was 47.0.

Below are given the results of a few experiments carried out with *N*-phen solutions and ethylene oxide in the absence of alkali:

Phenol.	Time, in hours.	Yield, Per cent.	$k = \frac{1}{t} \log \frac{x}{100(100-x)}$
Thymol .....	24	7.14	$32 \times 10^{-6}$
<i>p</i> -Cresol .....	2	1.01	61
2:4:6-Tribromophenol .....	2	2.7	139
2:4:6-Trichlorophenol .....	2	2.0	102
<i>p</i> -Nitrophenol .....	2	0.43	22
<i>o</i> -Nitrophenol .....	2	0.14	7



### Conclusions.

Directing attention in the first place to the results obtained in the case of ethylene oxide, the following conclusions may be drawn:

(1) The reactivity of the sodium phenoxide is enhanced by the presence of positive groups, for example,  $\cdot\text{CH}_3$ ,  $\cdot\text{C}_2\text{H}_5$ ,



and diminished by the presence of negative groups, for example,  $\cdot\text{OMe}$ ,  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ ,  $\cdot\text{Cl}$ ,  $\cdot\text{Br}$ ,  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{N}\cdot$ ,  $\cdot\text{CN}$ ,  $\cdot\text{NO}_2$ .

(2) Broadly speaking, it may be said that the speed of the reaction between ethylene oxide and the sodium phenoxide diminishes with increase in the acidity of the phenol. Exact data with regard to the relative acidities of the majority of phenols are, unfortunately, not available.

The following figures, however, bring out the general correctness of the foregoing statement:

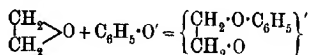
Phenol.	Hydrolysis of sodium salt at 25° V <sub>32</sub> (Hantzsch and Farmer).*	Velocity-constant of com- bination of sodium salt and ethylene oxide at 70°f.
Phenol .....	Per cent. 6.0	0.205
<i>p</i> -Chlorophenol .....	2.88	0.108
<i>o</i> -Chlorophenol .....	2.1	0.104
<i>p</i> -Hydroxybenzonitrile ...	0.52	0.026
2:4:6-Trichlorophenol.....	0.37	0.075
<i>p</i> -Benzeneazophenol .....	0.33	0.05
<i>p</i> -Nitrophenol .....	0.28	0.012

\* *Ber.*, 1899, 32, 3066, 3089.

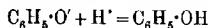
Of the seven phenols mentioned in the above list, five show a remarkably close agreement as regards the reactivity of the sodium salt towards ethylene oxide on the one hand and its tendency towards hydrolysis in aqueous solution on the other. The two exceptions are *p*-benzeneazophenol and 2:4:6-trichlorophenol. With regard to the former it is to be noticed that, as Hantzsch and Farmer point out, the method employed by them to determine the percentage of hydrolysis of the sodium salt, namely, hydrolysis of methyl acetate, is unsatisfactory in the case of this particular phenol, owing to its insolubility in water. A subsequent determination of the percentage of hydrolysis of the barium salt by Farmer by a different method (T., 1901, 79, 864) gave 0.90 at V<sub>32</sub> and 25°, a result which agrees well with the value found for the reactivity of the sodium salt towards ethylene oxide. 2:4:6-Trichlorophenol, on the other hand, stands out as a remarkable exception to the rule, the reactivity of its sodium salt towards ethylene oxide being five or six times as great as would be expected from the extent of its hydrolysis in aqueous solution.

This relationship between the speed of reaction of ethylene oxide

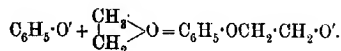
with the sodium derivative of a phenol and the acidity of the phenol finds a plausible explanation in the view already expressed that the process consists essentially in a combination of the olefine oxide with the phenoxy-ion:



Pronounced acidity on the part of a phenol implies a comparatively small tendency on the part of the phenoxy-ion to form an additive compound with a hydrogen ion; that is to say, it implies a considerable capacity on the part of the phenoxy-ion for stable independent existence in a suitable solvent. The *p*-cyanophenoxy-ion, to take one example, must be essentially a more stable grouping than the simple unsubstituted phenoxy-ion; and it seems not unreasonable to suppose that this stability would be exhibited, not only in relation to the hydrogen ion, but also in respect to other possible additive reactions, for instance, combination with an ethylene oxide molecule. In any case the facts appear to indicate that a certain analogy does exist between the two reactions:



and



(3) The reactivity of the sodium phenoxide depends on the positions of the substituent groups or atoms, as well as on their chemical nature; thus, thymol is considerably more reactive than the isomeric carvacrol, *p*-cresol than *o*-cresol. It is not possible, however, in the case of mono-substituted phenols to recognise any general rule connecting the position of a substituent and the magnitude of its effect on the reactivity of the sodium salt. In the four different *o*-, *m*-, and *p*-series which we have investigated, the order of reactivity is different in each case:

Cresols.		Chloro-phenols.		Hydroxy-benzo-nitriles.		Nitro-phenols.	
	<i>k</i> .		<i>k</i> .		<i>k</i> .		<i>k</i> .
<i>p</i> -	0.28	<i>p</i> -	0.108	<i>m</i> -	0.044	<i>m</i> -	0.032
<i>m</i> -	0.26	<i>o</i> -	0.104	<i>o</i> -	0.033	<i>p</i> -	0.012
<i>o</i> -	0.23	<i>m</i> -	0.101	<i>p</i> -	0.026	<i>o</i> -	0.0073

(4) The velocity-constants of 2:4:6-trichloro- and 2:4:6-tribromo-phenol give no indication of steric hindrance in the case of these phenols.

It would even appear from a consideration of the abnormal reactivity of sodium trichlorophenoxide already referred to, that two ortho-placed substituents, instead of hindering the combination

of the phenoxy-ion with the ethylene oxide molecule, actually favour it in some special way.

Turning now to the data in the case of propylene oxide, the following additional points may be noted:

(5) The speed of reaction between a sodium phenoxide and propylene oxide is always much lower than the speed of reaction between the same sodium phenoxide and ethylene oxide. In the case of phenol we have:

$$\frac{\text{Velocity constant for ethylene oxide}}{\text{Velocity constant for propylene oxide}} = \frac{0.075}{0.205} = 0.37,$$

and the ratio has approximately the same value for the majority of the less acidic phenols.

In the case of the more acidic phenols it has a higher value; for *p*-nitrophenol 0.58, for *m*-hydroxybenzonitrile 0.51. The highest value, 0.66, is reached in the case of 2:4:6-tribromophenol.

(6) The phenols stand, as regards the reactivity of their sodium salts, in almost the same order in the case of propylene oxide as in the case of ethylene oxide. The most notable exceptions are the trichloro- and tribromo-phenols,  $\alpha$ -naphthol and *o*-chlorophenol. These four phenols, two of which are ortho-substituted and the other two diortho-substituted, are much more reactive towards propylene oxide than would be expected from a consideration of the results obtained for the same phenols in the case of ethylene oxide. This is the more remarkable since in the case of ortho- and more especially in that of diortho-substituted phenols one might have anticipated a special retardation of the velocity as the result of the steric influence of the methyl group. Experiment shows, however, that precisely the opposite is the case. Instead of the reaction of the propylene oxide being retarded relatively to that of the ethylene oxide by the presence in a phenol of two ortho-substituents, it appears actually to be accelerated by the presence of these substituents.

(7) Very striking evidence in favour of the view that two ortho-placed substituents exert an accelerating influence on the reaction between olefine oxides and sodium phenoxides is found in the propylene oxide data for *p*-chlorophenol and 2:4:6-trichlorophenol. In spite of the much greater acidity of the trichlorophenol, its velocity-constant is as great as, if not greater than, that of *p*-chlorophenol.

(8) With regard to the results of the experiments in which ethylene oxide was heated with free phenols, it may be remarked that they show a qualitative agreement with the view that the formation of the glycol aryl ether depends on the combination of the ethylene oxide molecule with the phenoxy-ion. Thus, although,

is shown by the experiments with sodium phenoxides, the *p*-tolyl-oxy-ion is much more reactive than the trichlorophenoxy-ion, nevertheless, owing to the concentration of ions being much greater in the solution of free trichlorophenol than in that of *p*-cresol, the actual speed of formation of glycol aryl ether in the absence of alkali is greater in the case of trichlorophenol than in that of *p*-cresol.

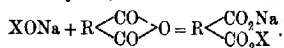
The velocity-constants of the free *o*- and *p*-nitrophenols also approach that of free *p*-cresol much more nearly than the constants for the sodium derivatives of the nitrophenols do that of sodium *p*-tolyl-oxy, as would be expected from the fact that the dissociation constants of the nitrophenols are greater than that of *p*-cresol.

(9) The experiments with benzeneazophenol show that the product obtained by the action of ethylene oxide on the sodium salt of this phenol is the same substance as is produced by the action of ethylene oxide on the free azophenol. This observation gives support to the view that the free azo-compound is present in aqueous alcoholic solution mainly, if not entirely, as a hydroxy-compound, and not to any considerable extent in the form of a quinone-hydrazone.

#### *Comparison of Results with those of Previous Investigations.*

Several investigations have in recent years been carried out with the object of determining the influence of substituents on the reactivities of phenols.

Schryver (T., 1899, 75, 661) investigated the behaviour of the sodium salts of a number of phenols towards the anhydride of camphoric acid, and found that in the majority of cases reaction takes place readily between the solid sodium salt and the camphoric anhydride dissolved in xylene, in accordance with the equation:

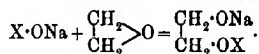
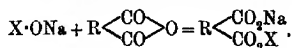


Two classes of substituted phenols proved, however, to be incapable of reacting with camphoric anhydride under the conditions employed by Schryver, namely, *o*- and *p*-nitrophenols and di-*o*-romphenols.

Although the sodium salt of *m*-nitrophenol reacts with a xylene solution of camphoric anhydride fairly readily at water-bath temperature, no reaction could be brought about between camphoric anhydride and the sodium salts of *o*- and *p*-nitrophenols, even on prolonged heating at 180°. Again, although reaction occurred readily between the xylene solution of camphoric anhydride and the sodium salts of 4-bromo- and 2:4-dibromo-phenol, no reaction

could be brought about between the camphoric anhydride solution and the sodium salts of 2:6-dibromo- and 2:4:6-tribromo-phenol even when the mixtures were heated in sealed tubes at 150—180°.

These results of Schryver with regard to *o*- and *p*-nitrophenols and the diortho-substituted phenols offer a remarkable contrast to our observations, a fact which is the more interesting since the two reactions appear at first sight to be distinctly similar in character:



It is to be noted, however, that whilst our experiments were carried out in alcoholic solution with the result that the reaction probably took place mainly, if not exclusively, between the phenoxylion and the olefine oxide molecule, in Schryver's experiments a solution of camphoric anhydride in xylene was allowed to act on the solid sodium salt of the phenol, and the reaction was probably limited almost entirely to the undissociated phenolic salt. Moreover, under the conditions employed by Schryver an important factor in determining the speed of reaction must necessarily be the solubility of the sodium salt in xylene, and it appears not impossible that this factor may have had some influence in producing the phenomena observed by him.

In the somewhat analogous case of the action of aqueous hydriodic acid on phenolic ethers it was found by Boyd and Pitman (T., 1905, 87, 1255) that 2:4:6-trichloro- and 2:4:6-tribromo-anisole showed an exceptional stability towards this reagent; but this stability is due in all probability merely to the insolubility of these ethers in the reagent, since it disappears when the hydriodic acid is allowed to act on them in a medium in which the ethers are soluble.

This solubility factor, unfortunately, also throws obscurity upon the meaning to be attached to the results obtained by Bischoff (Ber., 1900, 33, 1249) in an investigation of the action of the sodium salts of various phenols on  $\alpha$ -bromopropionic,  $\alpha$ -bromobutyric,  $\alpha$ -bromoisobutyric, and  $\alpha$ -bromoisovaleric esters.

The method of experiment consisted in boiling the sodium salt of the phenol with a solution of the bromo-ester in light petroleum for one hour, and determining the yield of phenoxy-derivative. Some of Bischoff's results differ to a remarkable extent from ours, as is shown by the following figures:

Phenol.	Yield of propionic ester derivative in one hour at 65—70°.	Yield of ethylene oxide derivative in two hours at 70.4°.
	Per cent.	Per cent.
Thymol .....	98	75
<i>o</i> -Cresol .....	95	64
Phenol .....	92	61
<i>p</i> -Cresol .....	62	72
<i>p</i> -Xylenol .....	59	68
$\psi$ -Cumenol ...	44	79
Guaiacol .....	40	54
<i>p</i> -Nitrophenol	0	5.6

Thus, whereas we find it to be an invariable rule that the introduction of one or more alkyl groups increases the reactivity of phenol, in several of Bischoff's experiments the reactivity of the alkyl-substituted phenol is less than that of phenol itself. Particularly striking is the case of  $\psi$ -cumenol, which Bischoff finds to be the least reactive of all the alkyl-substituted phenols investigated by him, but which we find to be the most reactive. It is, of course, the case that the reaction investigated by Bischoff is a double decomposition, whilst that studied by us is an additive reaction. Even this difference of character, however, would hardly have been expected to produce such entirely opposite results. Bischoff's observations on the retarding influence of negative groups, particularly nitro-groups, agree with our own.

Similar observations on the retarding influence of negative groups were made by Auwers and Haymann (*Ber.*, 1894, 27, 2795), who studied the action of ethyl chloroacetate in alcoholic solution on the sodium salts of certain phenols. Auwers and Haymann found, for example, that no reaction took place on digesting the sodium salts of *o*- and *p*-nitrophenol for thirty hours on a water-bath with an alcoholic solution of ethyl chloroacetate. The latter reaction has been re-investigated recently by Hewitt, Johnson, and Pope (*T.*, 1913, 103, 1626). These authors obtained a fair yield of ethyl *m*-nitrophenoxycetate by the action of ethyl chloroacetate in absolute alcoholic solution at water-bath temperature on the sodium salt of *m*-nitrophenol, but they were unable to isolate the isomeric ethyl *o*- and *p*-nitrophenoxycetates after treating the sodium salts of *o*- and *p*-nitrophenol in a similar way. From this result they draw the conclusion that in the sodium salts of *o*- and *p*-nitrophenol the grouping  $\text{:C:ONa}$  is wanting.

Our experiments, however, which show a steady gradation in the reactivities of the three nitrophenols, lend no support to the view that the sodium salts of *o*- and *p*-nitrophenol differ in constitution from the sodium salt of *m*-nitrophenol. The velocity-constants of reaction with ethylene oxide for the sodium salts of phenol and the three nitrophenols are as follows:

Phenol, 0.21; *m*-nitrophenol, 0.032; *p*-nitrophenol, 0.012; *o*-nitrophenol, 0.007.

The introduction of the  $\cdot\text{NO}_2$  group in the meta-position thus lowers the reactivity of phenol to about 1/7 of its value; the same group in the para-position reduces the reactivity to about 1/17, and in the ortho-position to about 1/30. Such differences are not greater than might naturally arise from the differences in the position of the  $\cdot\text{NO}_2$  group in the benzene nucleus.

Our results, of course, do not preclude the possibility that all three nitrophenols give rise to nitronic salts,  $\text{O}:\text{C}_6\text{H}_4\cdot\text{N}\begin{smallmatrix} \text{O} \\ \text{ONa} \end{smallmatrix}$  and that these react with the olefine oxides to produce nitronic esters which are quickly transformed into the more stable phenolic ethers.

#### EXPERIMENTAL.

As regards the method employed for the estimation of the glycol aryl ethers, one or two points in addition to those already mentioned on p. 2117 may be indicated.

In order to prevent any possibility of alcohol vapour catching fire during the process of sealing the reaction tube and so introducing carbon dioxide which would cause the precipitation of sodium carbonate, it was found advantageous to displace the air in the tube by means of nitrogen. It was found useful also to place in the reaction tube a small piece of glass rod, as this rendered the breaking of the bulb containing the olefine oxide much easier.

For the removal of the excess of phenol remaining after the reaction was over, a roughly normal solution of potassium hydroxide was employed.

In the majority of cases it was found necessary to shake seven or eight times with potassium hydroxide solution in order to remove the phenol completely. In certain cases, namely, those of thymol, carvacrol, *p*-xylenol, and  $\psi$ -cumenol, it was found impossible to extract all the free phenol by shaking an ethereal solution with aqueous potassium hydroxide.

The difficulty, however, was overcome by employing light petroleum (b. p. below  $50^\circ$ ) as the solvent for the glycol aryl ether, the excess of the phenol being then removed by six or eight shakings with aqueous potassium hydroxide. In order to prevent loss of glycol aryl ether in the aqueous solution, it was necessary to shake the series of alkaline liquors several times with fresh quantities of ether, or light petroleum, as the case might be. From 50 to 100 c.c. of ether were employed in the first extraction, and three or four portions, each of 50 c.c., in extracting the alkaline liquors, whilst

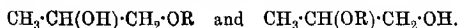
about 30 c.c. of aqueous potassium hydroxide were used in each washing. In commencing experiments with a new phenol, the last portion of ether was always evaporated separately, in order to ascertain if the extraction of the glycol aryl ether had been approximately complete. The following was found to be a convenient test for proving that the excess of phenol had been completely removed from the ethereal solution. Two or three c.c. of the last washing liquor were boiled to remove dissolved ether, then mixed with an equal volume of concentrated nitric acid, and boiled again for a few minutes. The liquid after cooling was mixed with excess of sodium hydroxide, when the solution acquired a brownish-yellow colour if phenol were present.

The greater part of the solvent used in extraction was evaporated in a water-bath, but in order to prevent possible loss of glycol ether by vaporisation, the last few c.c. were removed in a current of air.

Some of the glycol aryl ethers are hygroscopic, and, when oils, they were found to retain persistently small quantities of the solvent ether. Hence it was sometimes necessary to dry in a vacuum desiccator over sulphuric acid for several days before the weight became constant. In a few cases it was found that appreciable vaporisation takes place in a vacuum, and a constant loss of 1 to 3 milligrams in twenty-four hours was observed. In estimating the yields in these cases an allowance was made corresponding with the number of days during which the glycol ether had been drying, and the constant loss observed.

The majority of the aryl ethers obtained from ethylene oxide were crystalline substances, and of a high degree of purity, as was shown by analysis. The oily ethylene glycol ethers all readily gave crystalline *p*-nitrobenzoates, the purity of which was also ascertained by analysis.

The derivatives of propylene oxide, on the other hand, were, in the majority of cases, oils at the ordinary temperature, and in all cases appeared to consist of two compounds. The explanation of this fact is suggested by the following formulæ:



The quantities of the propylene glycol ethers prepared were small, and in no case enough to effect a complete separation of either constituent in sufficient amount to permit of a decision as to which of the two isomerides had been separated. In a few cases, however, one constituent proved to be so sparingly soluble in light petroleum that the other could be obtained in a state of purity by recrystallisation.

Usually a mixture of the two isomerides was analysed after one or two crystallisations, and the results of the analyses indicate that



the product of the action of propylene oxide on a sodium phenoxide consists entirely of substances having the empirical formula  $C_9H_6O_2R$ , in agreement with the view that a mixture of compounds having the above formula is in question.

In the case of propylene glycol 2:4:6-tribromophenyl ether a complete separation was effected. After repeated crystallisation from light petroleum, followed by crystallisation from dilute alcohol, three fractions were obtained, melting at 78—79°, 64—65°, and 42.5—43.5° respectively. The first and third fractions gave analyses agreeing with the composition  $C_9H_5O_2Br_3$ , the second was not analysed. It would appear that the first two are probably the isomeric ethers, whilst the third, the most soluble, is a eutectic mixture of these.

In view of the uncertainty as to which of the two isomerides is in question in those cases in which fractions having a sharp melting point were obtained, only typical ethers were analysed, sufficient to prove that the reaction proceeds as indicated, and that the products have the above empirical composition corresponding with one or both of the constitutional formulae given above.

The alcohol employed as solvent was commercial ethyl alcohol which had been boiled for some hours with solid sodium hydroxide and distilled. It had  $D_4^{20}$  0.79058, corresponding with 98.1 per cent. of ethyl alcohol. The presence of 2 per cent. of water made it possible to obtain  $N/20$ -solutions of the sodium salts of the nitrophenols, which are only sparingly soluble in absolute alcohol.

The  $N$ -phenol,  $N/20-Na$  solutions of the nitrophenols, were prepared in the reaction tubes by mixing standard solutions of the nitrophenols and sodium ethoxide in the proper proportions. In the case of *o*-nitrophenol a small quantity of the sodium salt separated at room temperature, but a clear solution was obtained at 70.4°. The  $N$ -phenol,  $N/20-Na$  solution of benzeneazophenol was prepared at 35° instead of at room temperature.

The ethylene oxide, after redistillation, boiled at 12.5—13°/757 mm.

The propylene oxide was prepared from propylene glycol by first converting this into the chlorohydrin by the action of sulphur chloride. The crude product was fractionated ten or twelve times, and the resulting liquid, boiling at 127—129°, was cautiously treated with concentrated aqueous potassium hydroxide and distilled. The crude propylene oxide so obtained was allowed to remain over potassium carbonate, distilled, and left in contact with metallic sodium to remove the last traces of water, and then repeatedly fractionated.

The treatment with sodium appeared to be necessary, as distilla-

tion over other dehydrating agents was not sufficient to remove the water. Unfortunately, the yield of propylene oxide was very much reduced by this treatment. Several other methods of preparation were tried, but the yield was even less satisfactory, and the product less pure. The fraction boiling at 34–36° under atmospheric pressure was used in the experiments.

The purity of the phenols was controlled by melting-point or boiling-point determinations.

#### Experimental Data.

The following examples of the experimental data obtained are given in full for illustrative purposes:

#### Phenol.

<i>Ethylene Oxide.</i>					<i>Propylene Oxide.</i>				
Time, hours.	Oxide, Gram.	Ether, Grams.	Yield, Per cent.	<i>k.</i>	Time, hours.	Oxide, Gram.	Ether, Gram.	Yield, Per cent.	<i>k.</i>
2	0.414	0.783	60.3	0.201	2	0.332	0.247	28.5	0.073
2	0.414	0.790	60.8	0.203	2	0.427	0.336	30.1	0.078
4	0.517	1.389	85.7	0.211	2	0.182	0.138	28.9	0.074
117(∞)	0.160	0.486	96.7		4	0.192	0.247	49.2	0.074
					48(∞)	0.123	0.299	92.7	

*Glycol phenyl ether p-nitrobenzoate* was prepared by treating a solution of the ether in pyridine with *p*-nitrobenzoyl chloride, the method followed being that described by Henderson and Heilbron (P., 1913, 29, 381). It crystallises from alcohol in needles melting at 63°.

In bulk the crystals showed a very pale yellow colour:

0.1961 gave 8.4 c.c.  $N_2$  (moist) at 19° and 767 mm.  $N=4.97$ .

$C_{15}H_{13}O_6N$  requires  $N=4.88$  per cent.

*Glycol o-tolyl ether*,  $C_7H_7 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , is a colourless oil boiling at 141°/19 mm. The *p*-nitrobenzoate crystallised from alcohol in colourless, iridescent plates, melting at 78.5–79.5°:

0.2172 gave 8.8 c.c.  $N_2$  (moist) at 16° and 771 mm.  $N=4.79$ .

$C_{10}H_{10}O_6N$  requires  $N=4.65$  per cent.

The mixture of isomeric *propylene glycol o-tolyl ethers* formed a yellow oil. The *p*-nitrobenzoates, after crystallisation from alcohol, formed white, microscopic crystals, melting between 78° and 84°:

0.2308 gave 9.4 c.c.  $N_2$  (moist) at 21° and 769 mm.  $N=4.68$ .

$C_{17}H_{17}O_6N$  requires  $N=4.45$  per cent.

*Glycol m-tolyl ether* was obtained as a colourless oil boiling at 145–147°/19 mm. The *p*-nitrobenzoate crystallised from alcohol in clusters of minute, colourless plates, melting at 80.5–81.5°:

0.2006 gave 8.3 c.c.  $N_2$  (moist) at  $14^\circ$  and 760 mm.  $N=4.87$ .

$C_{10}H_{15}O_3N$  requires  $N=4.65$  per cent.

*Glycol p-tolyl ether* crystallises from hot light petroleum in colourless prisms, melting at  $44-45^\circ$ :

0.1666 gave 0.4331  $CO_2$  and 0.1187  $H_2O$ .  $C=70.89$ ;  $H=7.97$ .

$C_9H_{12}O_2$  requires  $C=71.01$ ;  $H=7.96$  per cent.

*Glycol p-xylyl ether*,  $C_8H_9\cdot O\cdot CH_2\cdot CH_2\cdot OH$ , crystallises from hot light petroleum (b. p.  $40-65^\circ$ ) in clusters of fine needles melting at  $46^\circ$ :

0.1488 gave 0.3939  $CO_2$  and 0.1126  $H_2O$ .  $C=72.19$ ;  $H=8.48$ .

$C_{10}H_{14}O_2$  requires  $C=72.23$ ;  $H=8.51$  per cent.

*Glycol  $\psi$ -cumyl ether*,  $C_9H_{11}\cdot O\cdot CH_2\cdot CH_2\cdot OH$ , crystallises from light petroleum in colourless, prismatic crystals, melting at  $70-71^\circ$ :

0.1390 gave 0.3736  $CO_2$  and 0.1116  $H_2O$ .  $C=73.28$ ;  $H=9.00$ .

$C_{11}H_{16}O_2$  requires  $C=73.24$ ;  $H=8.97$  per cent.

Since this ether is not very readily soluble in cold light petroleum a mixture of light petroleum with a small quantity of ordinary ether was used as the extracting solvent in the experiments on the velocity of reaction.

*Glycol 3-methyl-6-isopropylphenyl ether*,  $C_{10}H_{13}\cdot O\cdot CH_2\cdot CH_2\cdot OH$ , remained as an almost colourless oil on evaporation of the light petroleum used as extracting solvent. Some months later it spontaneously crystallised on being poured from one vessel to another, forming a white, crystalline mass. It was dissolved in hot light petroleum (b. p.  $68-73^\circ$ ), from which, on seeding the cold solution, it separated in transparent prisms melting at  $53-54^\circ$ :

0.2097 gave 0.5687  $CO_2$  and 0.1739  $H_2O$ .  $C=73.96$ ;  $H=9.29$ .

$C_{12}H_{18}O_2$  requires  $C=74.16$ ;  $H=9.36$  per cent.

The mixture of isomeric *propylene glycol 3-methyl-6-isopropylphenyl ethers* formed a yellow, viscous oil. The *p-nitrobenzoates* formed a pasty mass completely soluble in light petroleum, from which crystals slowly separated on evaporation of the solvent. The crystals were drained from oil on a porous plate, and recrystallised from alcohol. In this way the less soluble isomeride was obtained in pale yellow crystals melting at  $60.5-62^\circ$ :

0.4570 gave 16.1 c.c.  $N_2$  (moist) at  $21^\circ$  and 762 mm.  $N=4.02$ .

$C_{20}H_{23}O_3N$  requires  $N=3.92$  per cent.

*Glycol 2-methyl-5-isopropylphenyl ether*,

$C_{10}H_{13}\cdot O\cdot CH_2\cdot CH_2\cdot OH$ ,

separates from light petroleum (b. p.  $40-60^\circ$ ) in silky needles melting at  $51-52^\circ$ :

0.1407 gave 0.3830  $\text{CO}_2$  and 0.1174  $\text{H}_2\text{O}$ .  $\text{C}=74.25$ ;  $\text{H}=9.36$ .

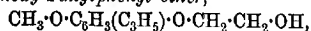
$\text{C}_{12}\text{H}_{18}\text{O}_2$  requires  $\text{C}=74.16$ ;  $\text{H}=9.36$  per cent.

*Glycol o-methoxyphenyl ether*,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , was obtained as a colourless oil boiling at  $166-167^\circ/22$  mm. On remaining it slowly changed to a mass of deliquescent, white crystals with a low melting point. The *p*-nitrobenzoate separated from alcohol in rosettes of white crystals melting at  $87-88^\circ$ :

0.1919 gave 7.5 c.c.  $\text{N}_2$  (moist) at  $14^\circ$  and 749 mm.  $\text{N}=4.53$ .

$\text{C}_{16}\text{H}_{18}\text{O}_6\text{N}$  requires  $\text{N}=4.42$  per cent.

*Glycol 2-methoxy-4-allylphenyl ether*,



dissolves very readily in ether, benzene, alcohol, or ethyl acetate. It was recrystallised by dissolving in dry ether and adding to the solution sufficient light petroleum to produce a slight turbidity. On cooling the turbid liquid in a freezing mixture, the substance separated quickly in colourless needles, melting at  $36-37^\circ$ :

0.1392 gave 0.3518  $\text{CO}_2$  and 0.0965  $\text{H}_2\text{O}$ .  $\text{C}=68.93$ ;  $\text{H}=7.77$ .

$\text{C}_{12}\text{H}_{16}\text{O}_3$  requires  $\text{C}=69.18$ ;  $\text{H}=7.76$  per cent.

*Glycol  $\alpha$ -naphthyl ether*,  $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , was obtained as a red, crystalline mass. It was purified from small quantities of colouring matter by extracting the crude product repeatedly with light petroleum. On cooling the petroleum solution the glycol ether separated as an oil, which solidified on rubbing with a crystal. It was then dissolved in dry ether, in which it is very readily soluble, and to this solution light petroleum was added until a faint opalescence was produced.

A crystal of the glycol ether was then introduced, and the solution left for some time, when clusters of minute, colourless plates separated, which melted at  $42^\circ$ :

0.1450 gave 0.4054  $\text{CO}_2$  and 0.0836  $\text{H}_2\text{O}$ .  $\text{C}=76.26$ ;  $\text{H}=6.46$ .

$\text{C}_{12}\text{H}_{12}\text{O}_2$  requires  $\text{C}=76.56$ ;  $\text{H}=6.44$  per cent.

The mixture of isomeric *propylene glycol  $\alpha$ -naphthyl ethers* formed an oil which slowly solidified to a mass of pink crystals. These were moderately soluble in boiling light petroleum, and from this solution one of the ethers separated as a woolly mass of needles melting at  $64-65^\circ$ , the other being left as an oil.

*Glycol  $\beta$ -naphthyl ether* was obtained as a crystalline solid with a slightly pink colour. It was recrystallised twice from hot benzene, from which it separated as an almost colourless, crystalline powder, melting at  $76^\circ$ :

0.1667 gave 0.4669  $\text{CO}_2$  and 0.0964  $\text{H}_2\text{O}$ .  $\text{C}=76.38$ ;  $\text{H}=6.48$ .

$\text{C}_{12}\text{H}_{12}\text{O}_2$  requires  $\text{C}=76.56$ ;  $\text{H}=6.44$  per cent.

The mixture of isomeric *propylene glycol  $\beta$ -naphthyl ethers* con-

sisted of pink crystals. Crystallisation from dilute alcohol, followed by crystallisation from light petroleum, gave a colourless fraction melting at 80–82°:

0.1290 gave 0.3629 CO<sub>2</sub> and 0.0825 H<sub>2</sub>O. C=76.72; H=7.16.

C<sub>13</sub>H<sub>14</sub>O<sub>3</sub> requires C=77.19; H=6.98 per cent.

*Glycol o-chlorophenyl ether*, C<sub>6</sub>H<sub>4</sub>Cl·O·CH<sub>2</sub>·CH<sub>2</sub>·OH, was obtained as a colourless oil boiling at 159–161°/22 mm. The *p-nitrobenzoate* crystallises from alcohol in small, transparent plates, with a pale yellow tinge and melting at 81–82°:

0.1944 gave 7.3 c.c. N<sub>2</sub> (moist) at 18° and 768 mm. N=4.38.

C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>NCl requires N=4.36 per cent.

*Glycol m-chlorophenyl ether* is a colourless oil boiling at 163–164°/22 mm. The *p-nitrobenzoate* crystallises from alcohol in small, dense crystals with a very pale yellow tint, and melting at 104°:

0.1672 gave 6.2 c.c. N<sub>2</sub> (moist) at 17° and 768 mm. N=4.35.

C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>NCl requires N=4.36 per cent.

The mixture of isomeric *propylene glycol m-chlorophenyl ethers* formed an oily liquid. The *p-nitrobenzoates*, after repeated crystallisation from light petroleum and from alcohol, were partly separated. The specimen analysed melted at 98.5–101°:

0.2129 gave 8.1 c.c. N<sub>2</sub> (moist) at 15° and 738 mm. N=4.33.

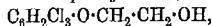
C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>NCl requires N=4.18 per cent.

*Glycol p-chlorophenyl ether* was obtained as an almost colourless, crystalline mass, melting at about 28°. The *p-nitrobenzoate* crystallises from alcohol in needles with a very pale yellow tinge, and melting at 90–91°:

0.1729 gave 6.5 c.c. N<sub>2</sub> (moist) at 18° and 766 mm. N=4.38.

C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>NCl requires N=4.36 per cent.

The *glycol 2:4:6-trichlorophenyl ether*,



was crystallised from hot light petroleum (b. p. 68–75°), from which it separates in prismatic needles melting at 77°:

0.1946 gave 0.3471 AgCl. Cl=44.13.

C<sub>6</sub>H<sub>2</sub>O<sub>2</sub>Cl<sub>3</sub> requires Cl=44.08 per cent.

*Glycol 2:4:6-tribromophenyl ether*, C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·O·CH<sub>2</sub>·CH<sub>2</sub>·OH crystallises from hot ethyl alcohol in fine needles melting at 116°:

0.1710 gave 0.2583 AgBr. Br=64.27.

C<sub>6</sub>H<sub>2</sub>O<sub>2</sub>Br<sub>3</sub> requires Br=63.97 per cent.

The mixture of isomeric *propylene glycol 2:4:6-tribromophenyl ethers* by repeated crystallisation, first from light petroleum and afterwards from dilute alcohol, was separated into three fractions

melting at 78—79°, 64—65°, and 42·5—43·5° respectively. The first and third fractions were analysed:

I. 0·0867 gave 0·1263 AgBr. Br=61·96.

III. 0·1402 „ 0·2031 AgBr. Br=61·64.

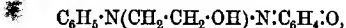
$C_9H_9O_2Br_3$  requires Br=61·67 per cent.

*Glycol p-benzeneazophenyl ether*,  $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , crystallises from benzene in orange-coloured needles melting at 100°:

0·1231 gave 12·4 c.c.  $N_2$  (moist) at 14° and 759 mm. N=11·84.

$C_{14}H_{14}O_2N_2$  requires N=11·57 per cent.

In order to ascertain whether benzeneazophenol, in the absence of alkali, would react with ethylene oxide as a quinone-hydrazone, producing a derivative of the formula



a solution of the free phenol was heated with ethylene oxide for some hours. Since it has been shown by Knorr (*Ber.*, 1899, **32**, 729) that ethylene oxide does not react easily with amines in the absence of water, the solvent employed in this case was a mixture of alcohol and water in about equal proportions by volume. The product under these conditions was quite similar in appearance to the substance produced when alkali was present, and had the same melting point. A mixture of the two products in about equal proportions also melted at the same temperature.

It would appear, therefore, that the same substance, namely, that of the formula  $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , was produced in each case.

The mixture of isomeric *propylene glycol benzeneazophenyl ethers* consisted of orange crystals, sparingly soluble in light petroleum. This solvent readily effects a separation of the two ethers, the more soluble isomeride crystallising with difficulty. The specimen analysed melted at 99—101·5°:

0·1970 gave 18·3 c.c.  $N_2$  (moist) at 12° and 751 mm. N=10·86.

$C_{15}H_{16}O_2N_2$  requires N=10·94 per cent.

*Glycol o-cyanophenyl ether*,  $CN \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , was obtained as a colourless oil boiling at 203°/19 mm. The *p-nitrobenzoate* separates from alcohol in almost colourless, minute, prismatic crystals, melting at 108°:

0·1913 gave 14·7 c.c.  $N_2$  (moist) at 16° and 766 mm. N=9·03.

$C_{16}H_{12}O_5N_2$  requires N=8·98 per cent.

*Glycol m-cyanophenyl ether* was crystallised by dissolving it in pure dry ether, and adding to the solution sufficient light petroleum to produce an opalescence. The glycol ether separated slowly in colourless, microscopic crystals, melting at 52—53°:

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0.1467 gave 10.7 c.c.  $N_2$  (moist) at  $12^\circ$  and 760 mm.  $N=8.66$ .

$C_9H_9O_2N$  requires  $N=8.59$  per cent.

*Glycol p-cyanophenyl ether* crystallises from benzene in prismatic needles, melting at  $86^\circ$ :

0.1437 gave 10.6 c.c.  $N_2$  (moist) at  $12^\circ$  and 750 mm.  $N=8.64$ .

$C_9H_9O_2N$  requires  $N=8.59$  per cent.

The mixture of isomeric *propyleneglycol p-cyanophenyl ethers* formed a yellow, viscous oil, which crystallised, on long keeping, in almost colourless needles melting between  $46^\circ$  and  $67^\circ$ :

0.2911 gave 20.75 c.c.  $N_2$  (moist) at  $21^\circ$  and 764 mm.  $N=8.16$ .

$C_{10}H_{11}O_2N$  requires  $N=7.91$  per cent.

*Glycol o-nitrophenyl ether*,  $NO_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ , was obtained as a yellow oil, which solidified after keeping for some days. It was crystallised by dissolving in cold ethyl acetate and adding to the solution sufficient light petroleum to produce an opalescence. On introducing a crystal of the substance into the solution cooled in a freezing mixture, a rapid separation of the ether in small, but well-defined, transparent prisms took place. In bulk the crystals had a distinct, although pale, yellow colour; they melted at  $35-36^\circ$ :

0.1732 gave 11.4 c.c.  $N_2$  (moist) at  $15^\circ$  and 766 mm.  $N=7.78$ .

$C_8H_9O_4N$  requires  $N=7.65$  per cent.

*Glycol m-nitrophenyl ether*, in the crude state, formed crystals with a very pale yellow tinge. It was recrystallised by dissolving in cold ethyl acetate and adding light petroleum to the solution, when almost colourless, prismatic crystals separated, melting at  $87-88^\circ$ :

0.0929 gave 6.0 c.c.  $N_2$  (moist) at  $12.5^\circ$  and 778 mm.  $N=7.81$ .

$C_8H_9O_4N$  requires  $N=7.65$  per cent.

*Glycol p-nitrophenyl ether* was obtained in almost colourless crystals melting at  $92-94^\circ$ , but giving a turbid liquid, which did not become clear until about  $100^\circ$ . In spite of several recrystallisations it was not found possible to obtain a specimen with a sharp melting point. The temperature of fusion of the crystals varied slightly according as benzene, alcohol, or ethyl acetate was employed as the solvent. The sample analysed had been crystallised by dissolving in cold ethyl acetate and adding light petroleum. It formed almost colourless, prismatic needles, softening at  $84^\circ$  and melting at  $89-92^\circ$ :

0.1614 gave 10.4 c.c.  $N_2$  (moist) at  $11^\circ$  and 757 mm.  $N=7.66$ .

$C_8H_9O_4N$  requires  $N=7.65$  per cent.

The mixture of *propylene glycol p-nitrophenyl ethers* formed a

brown oil, from which one of the isomerides slowly separated in pale yellow, transparent prisms.

These were soluble in hot light petroleum, and on cooling a pale yellow oil separated, which slowly crystallised in large, clear, amber prisms, melting at 65—68°. The crystals were pressed to remove adhering brown oil, and recrystallised from light petroleum, when they melted at 71°:

0.2263 gave 14.15 c.c.  $N_2$  (moist) at 16° and 769 mm.  $N=7.38$ .

$C_9H_{11}O_4N$  requires  $N=7.11$  per cent.

The mixture of isomeric *propylene glycol m-dimethylaminophenyl ethers* formed a dark-coloured oil, showing signs of incipient crystallisation. An aqueous solution of the *hydrogen oxalates* of the ethers was evaporated under diminished pressure over sulphuric acid, and the residue was crystallised from alcohol. In this way the hydrogen oxalate of one of the isomerides was obtained in white crystals, melting at 133—134°:

0.1913 gave 8.35 c.c.  $N_2$  (moist) at 16° and 764 mm.  $N=5.12$ .

$C_{11}H_{17}O_2N_2C_2H_2O_4$  requires  $N=4.91$  per cent.

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### CXCVII.—*The Osmotic Properties and Physical Constitution of Caoutchouc Solutions.*

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THE osmotic pressures exerted against a semi-permeable diaphragm by various colloids in aqueous solution have been frequently determined, and the results in many cases have been of considerable interest. The real significance, however, of the osmotic rise of a colloidal solution—assuming equilibrium to have been experimentally attained—is often a matter of some dubiety. Not only is the condition of such a solution liable to variation with age, temperature, mode of preparation, and other factors, but additional complications, into which it is unnecessary here to enter, are introduced by the inevitable presence of small quantities of foreign electrolytes or by the partial ionisation of the colloid itself. When, as in the present experiments, the solvent is a non-ionising organic liquid, matters are simplified in so far as electrolytic complications may be disregarded. On the other hand, those colloidal solutions which,



like those of caoutchouc, are extremely viscid at concentrations of a few per cent., are clearly different in their constitution from solutions of crystalloids and from the numerous colloidal solutions approximating in their habit to those of crystalloids, all of which have viscosities increasing only slightly more rapidly than the concentration until very high concentrations are reached. It cannot, therefore, be surprising if solutions of the caoutchouc type show peculiarities of their own when their osmotic pressure is measured by the direct method.

Osmotic measurements are usually undertaken with the aim of ascertaining the molecular weight of the dissolved substance. It has been shown by Perrin (*Compt. rend.*, 1908, **146**, 967; 147, 594) that particles large enough to be microscopically visible obey, when suspended or emulsified in a liquid, the osmotic laws of Raoult and van't Hoff in the same way as crystallised substances in molecular solution, and there is no reason to suppose that freely moving particles of dissolved substance in a colloidal sol behave otherwise, no matter whether the particles be large or small, liquid or solid, or whether the sol be transparent or opalescent, mobile or viscid. Provided, therefore, that the colloidal particles be not too large to show any osmotic effect measurable by the ordinary methods, and that the osmotic phenomena be not too much blurred by the superimposition of effects not ascribable to osmotic pressure in the strict sense, conclusions may be legitimately drawn as to the mean size and mass of the particles. Even then the quantities so found correspond only with the particles actually existing in solution, which in the nature of things are much more likely to be highly associated than the mainly unimolecular particles of dissolved crystalloids. In other words, the deduction of molecular weight from osmotic data is least likely to be illusory when the colloidal solutions approach those of crystalloids in their general properties and when they follow the Raoult-van't Hoff relation in regard to concentration and temperature-coefficient.

As regards the measurement of osmotic quantities, the cryoscopic and ebullioscopic methods, although they have from time to time been applied to colloids, have usually failed to yield any precise information, partly because they are not delicate enough to cope with the very large molecules concerned, and partly because impurities exert their full effect. By direct measurement of the pressure inside a semi-permeable septum, a higher delicacy is obtained (10 cm. of benzene correspond with  $0.018^\circ$  of cryoscopic depression), whilst the latter source of error is largely obviated by the permeability of the diaphragm to impurities of comparatively low molecular weight. With caoutchouc, the depression of freezing

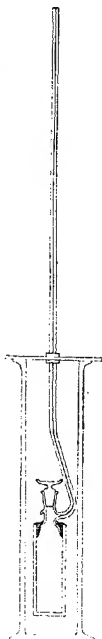
point in benzene solution is so small (Gladstone and Hibbert, *Phil. Mag.*, 1889, [v], 28, 38) as to be of little quantitative value. It therefore seemed not uninteresting to investigate the osmotic pressure of caoutchouc solutions by the direct method.

#### EXPERIMENTAL.

The solvents employed were benzene and light petroleum (b. p. 80–120°). For a semi-permeable diaphragm it was found, after trials of various materials, that ordinary cylindrical cells of white porous earthenware served very well. These cells, when free from concealed flaws or isolated large pores, retained the more viscous caoutchouc solutions very successfully, whilst permitting a free passage of solvent; with thin solutions, however, their semi-permeability proved to be somewhat uncertain. Consequently it was found desirable to block the pores of the cells, in the manner described below, with cold-vulcanised caoutchouc, which is impermeable towards dissolved caoutchouc and, in thin layers, tolerably permeable towards solvent. The dimensions of the cells were: height, 75 mm.; diameter, 25 mm.; thickness of wall, 3 mm.; the capacity of the osmometer when fitted up was about 25 c.c.

Three forms of osmometer, adapted to dilute, intermediate, and concentrated solutions, were used. The intermediate form (Fig. 1) had a short, wide glass tube of 10 mm. bore, closed by a well-ground stopper, cemented into the cell. The manometer-stalk, consisting of thick-walled tubing of about 1 mm. bore and 40–50 cm. length, was sealed in laterally. With this type of osmometer the charging of the cell was greatly facilitated, whilst leakage of solution past the stopper could be effectually prevented by smearing the latter with glucose-syrup and clamping it down by means of springs. Owing to the narrow bore of the manometer, a correction for capillarity (5 to 10 mm.) had to be subtracted from all readings. As thus constructed, the osmometer was not well suited to the reading of pressure-heads amounting to but a few cm.; for very dilute solutions, therefore, a simpler form was adopted, having a straight glass stalk of 4 mm. bore and 20 cm. length, cemented directly into the cell. A disadvantage of this type was that small movements of head in the stalk involved the inward or outward diffusion of somewhat large quantities of solvent; it was accordingly

FIG. 1.



reserved for cases where the eventual position of the meniscus was approximately known at the outset. For concentrated solutions giving pressures, in terms of solution, of 50 cm. or more, mercury osmometers were used differing from the first-named type only in that the short lateral tubulure was bent downwards and then upwards, and carried a small reservoir in the shorter arm.

In order to fix the glass parts into the cell, the lower end of the inserted tube was continued by a short piece not much narrower than the bore of the cell itself, and trumpeted out so as to pass in with a little friction. A stiff paste of powdered asbestos and syrupy sodium silicate was worked into the interstitial space and slightly banked up on the outside. The cement was allowed to harden for at least twenty-four hours, and the apparatus was then heated for several hours in a drying oven. It was observed that the trustworthiness of the joint depended on keeping the annular space between glass and cell as narrow as possible.

The glass parts having been attached, the cells were filled with a 10 per cent. solution of deviscified caoutchouc in benzene and immersed in the same liquid, and were placed under diminished pressure. After the air included in the pores had thus been extracted, the apparatus was left to itself under the ordinary pressure for some hours, so that the cells might be fully impregnated with caoutchouc solution. They were then immersed, inside and out, in a 3 per cent. solution of sulphur monochloride in benzene, whereby the caoutchouc taken up was vulcanised; finally, they were washed by repeated soaking in fresh benzene.

The cells were held, by means of perforated ground-glass disks, in ordinary gas-cylinders containing the outer solvent. The cylinders were kept in a thermostat at 25°. Readings of the manometric columns were carried out in some cases by means of paper scales gummed to the stalks, in others by the aid of a rigid, movable scale. Before beginning an experiment, the inner and outer liquids were brought to a temperature of 25° in order to avoid "thermometer effect," that is, initial rise in the manometer due to thermal expansion. With the stoppered osmometers this was easily effected by charging and fitting up the osmometer, without inserting the stopper, and keeping it in this condition for an hour in the thermostat before securing the stopper in position.

With osmometers having a capillary manometer, the rise of liquid in the latter became perceptible very soon after closure, and proceeded, in general, at a rate of 2–3 cm. (of organic liquid) per hour during the first few hours; the rate, as might be expected, varied not only with the solution, but also with the particular osmometer employed. In the neighbourhood of equilibrium the

rise slowed down to 1—2 cm. per day, or less. At this stage the manometer column, unless the cell were leaky or the solution losing viscosity very rapidly, remained constant within a few mm. for several days, and then underwent a slow and steady fall corresponding with the spontaneously decreasing viscosity of the solution.

Before the connexion between viscosity and osmotic rise had become apparent, this fall seemed to indicate leakiness of the cells. Genuine cases of leakiness, however, were readily detected by the abnormally rapid fall in the manometric stalk when the osmometer was charged inside and out with pure solvent. Some forms of caoutchouc which lose viscosity in solution more rapidly than others were rejected; with the pale plantation crape used for the present experiments, the rate of manometric fall due to this cause ranged from 1 to 3 mm. per day.

Pressure-equilibrium in the osmometers was frequently put to the test by lowering or raising the level of the liquid in the manometer. With capillary stalks, the original level was always restored to within a few mm. in the course of half a day, from either side. With wide stalks the return, as might be expected, was too slow to be complete within reasonable time. Transpiration of caoutchouc through the cell-walls was controlled from time to time by analysis of the outer liquid. In no case (apart from demonstrably leaky cells) were more than 1.5 grams of caoutchouc per litre found in solution, which quantity may be considered negligible. Moreover, no change in the manometric column was ever noted as the result of substituting fresh solvent for the outer liquid.

Solutions of caoutchouc were prepared at the highest concentration at which they were intended to be used, and a series of less concentrated solutions was made by diluting the original one. Osmometric readings were taken as soon as possible after the manometric column had been observed to reach equilibrium, and the actual concentration of the solution was then determined, as also its viscosity. The latter was determined at 20° by the capillary-flow method in an Ostwald viscometer; the same instrument was used throughout, the times of efflux being for pure benzene seventeen seconds and for pure light petroleum sixteen seconds.

Table I shows the osmotic rises and viscosities of a series of benzene solutions of deresinified plantation rubber, containing in suspension nitrogenous and mineral matter to the extent of 3 per cent. of the rubber, and having only a slight opalescence. The figures under *c* represent grams of substance in 100 c.c. of solution, *H* the manometric column in millimetres as read off, *H'* the same calculated to atmospheres, *V* the viscometric time of efflux.

TABLE I.  
(*Fresh Caoutchouc, Benzene.*)

<i>c.</i>	<i>H.</i>	<i>H'</i>	<i>V.</i>
5.26	45 (mercurey)	0.0592	—
3.59	360	0.0307	—
2.92	251	0.0214	—
2.10	137	0.0117	3196"
1.48	77	0.0066	989
1.01	42	0.0036	374

On comparing *c* with *H*, it will be seen that the osmotic rise increases far more rapidly than the concentration. The manner in which the *c*—*H* curve turns upward has something in common with the well-known trend of the curves connecting the viscosity of caoutchouc solutions with their concentration, and for this reason the one curve was always, in the present experiments, compared with the other.

The parallelism between osmotic rise and viscosity was confirmed in other ways. Solutions of caoutchouc invariably undergo a slow diminution of viscosity on keeping, which diminution can be artificially hastened by heat or light. When a portion of the same solution as in table I had thus been partly deviscified, the following figures were obtained.

TABLE II.  
(*Partly Deviscified Caoutchouc, Benzene.*)

<i>c.</i>	<i>H.</i>	<i>H'</i>	<i>V.</i>
4.45	275	0.0235	771"
3.37	185	0.0158	402
2.70	136	0.0116	285
2.17	105	0.0088	213
1.04	42	0.0036	86

Here it is seen that solutions of the same material and the same concentration vary in osmotic effect *pari passu* with the viscosity, independently of the concentration. A further series of experiments was made with caoutchouc deviscified to an extreme point by boiling the solution for more than eighty hours. The condition of the caoutchouc then isolated by evaporation was that of a treacly and exceedingly adhesive mass almost destitute of elasticity. Resinous oxidation-products were extracted by shaking the solution repeatedly with 95 per cent. alcohol; nevertheless, owing to residual traces of such impurities, the osmotic rises at first went considerably beyond the eventual position of equilibrium. In order to allow for this, the column was lowered by the aid of a capillary pipette after twenty-four hours' keeping, and the experiment thus started afresh. The results were as follows:

TABLE III.

(Highly Deviscified Caoutchouc, Benzene.)

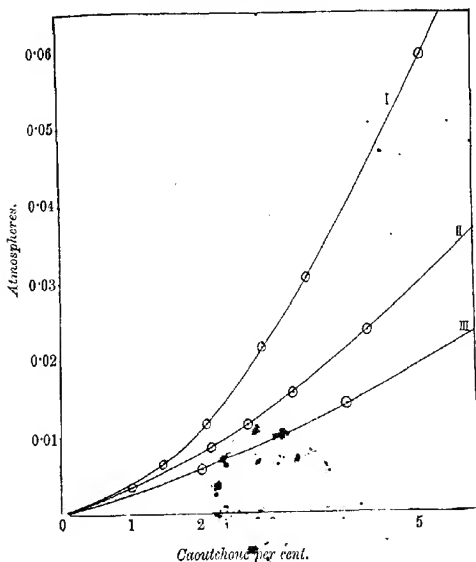
C.	H.	$\frac{C}{H}$	$\frac{C}{H}$
9.95	37 (mercury)	0.0487	287
6.89	330	0.0252	150
4.11	165	0.0141	68
2.06	71	0.0060	35

A graphic conspectus of all the results with benzene solution is given in Figs. 2 and 3.

Similar series of determinations with solutions of the same

FIG. 2.

Osmotic rises in benzene.



caoutchouc in light petroleum gave the results tabulated below. These solutions were strongly opalescent, and showed, in concentrations of 1.5 per cent. and more, a much more strongly marked ropiness, or elastic viscosity, than benzene solutions. This difference evidently corresponds with the greater ease with which the pectous constituent of raw india rubber (see *J. Soc. Chem. Ind.*,

1913, 32, 1041) dissolved in benzene than in paraffin hydrocarbons.

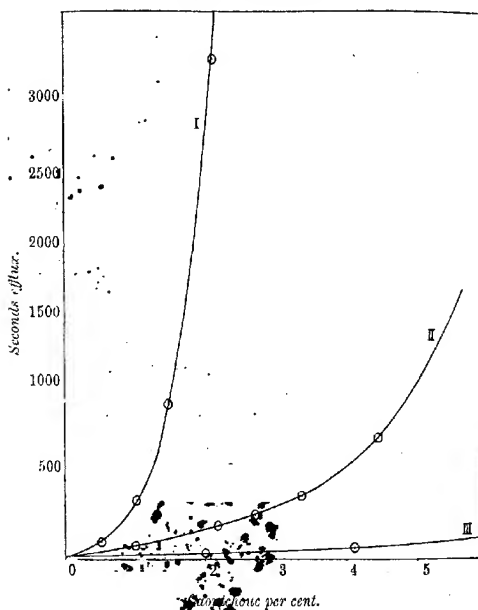
TABLE IV.

(Partly Dissolved in Benzene, Light Petroleum.)

		$H'$	$V$
	394	0.0282	—
	246	0.0176	11330
1.78	130	0.0093	960
0.99	51	0.0036	285
0.50	22	0.0016	102

FIG. 3.

Viscosities in benzene.



(Partly Dissolved in Benzene, Light Petroleum.)

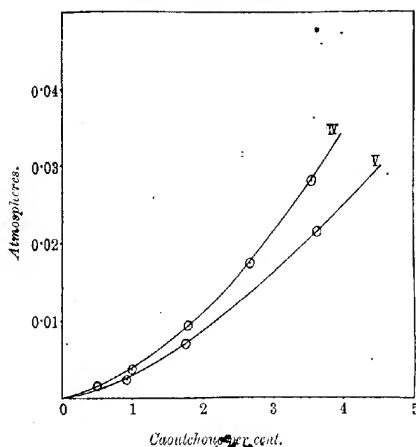
$c$	$H'$	$V$
3.63	0.0218	564
1.76	0.0070	138
0.91	0.0024	60

Here, again, the osmotic rise is seen to depend largely on the physical condition of the solution, a fact from concentration. With solutions of about the same degree of fractionation (comparable to I and IV), the osmotic rises in benzene and light petroleum solution are not very different. The curves for light petroleum solutions are given in Figs. 4 and 5.

Finally, in order to demonstrate still more clearly the influence of the physical condition of solutions, osmometers were set up with solutions of the same material and concentration on either side of the septum, differing only in viscosity. The devised solutions

FIG. 4.

*Osmotic rises in light petroleum.*



constituted the outer liquid. The more viscous solutions invariably showed an osmotic rise against the less viscous, as is apparent from the following figures:

TABLE VI

Benzene:

c inner.	c outer.
2.51	2.49
1.99	2.02

c inner.	c outer.	Rise.
2.51	2.49	261 mm.
1.99	2.02	150

Light petroleum:

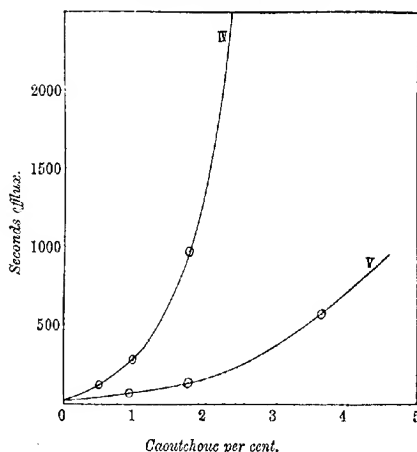
c inner.	c outer.
4.13	4.07
2.02	2.00

c inner.	c outer.	Rise.
4.13	4.07	316 mm.
2.02	2.00	112



It further seemed of interest to determine the osmotic rise of gutta-percha solutions. Washed gutta-percha was freed from resin as far as possible by extraction with acetone, and from mechanical impurities by filtration of the solution. Owing to the presence of residual traces of resin, the first rises were in most of the experiments abnormally high; the same procedure, therefore, was adopted as in the case of highly deviscified caoutchouc. The following

FIG. 5.  
*Viscosities in light petroleum.*



results were obtained with benzene as solvent. In column *M* the molecular weight, as calculated by the van't Hoff relation, is shown.

TABLE VII.  
(Gutta-percha, Benzene.)

<i>c.</i>	<i>H.</i>	<i>H.</i>	<i>V.</i>	<i>M.</i>
6.03	38 (mercury)	0.0500	270	29500
3.04	279	0.0238	81	31100
2.04	171	0.0146	45	34000
1.26	101	0.0088	35	35600

It appears from the above experiments that the osmotic rise of caoutchouc solutions against their solvent at a given temperature is by no means purely a function of the concentration, but depends largely on the physical condition of the solutions. This phenom-

menon is evidently connected with their colloidal nature, and may well, in a greater or less degree, be common to all colloidal solutions.

If the rises are regarded as due solely to osmotic pressure proper, the anomalous relations between osmotic rise and concentration can only be set down to variations in the mean size of the molecule. The effects of co-volume and of intermolecular attraction cannot, at such low concentrations, account for  $c-H$  curves so strongly curved as those of tables I and IV. There must, then, in a given viscoid solution of caoutchouc be a predominance of large, highly associated molecules at lowest concentrations, and a rapidly increasing dissociation as the concentration rises. Also, in a solution of given concentration, molecular association must increase as the viscosity decreases. These conclusions, however, are directly opposed to what is known of the general relations existing between concentration, molecular association, and viscosity.

A more probable explanation would seem to lie in the colloidal characteristics of caoutchouc and the two-phase constitution of its solutions. There can hardly be any doubt that solutions of caoutchouc, like those of gelatin (see Garrett, *Phil. Mag.*, 1903, [vi], 6, 374), are composed of a sol-phase and a gel-phase, the latter of which, although uniformly dispersed in the former, has sufficient cohesion of its own to impart a certain elasticity to the solution. The ropy habit of moderately dilute caoutchouc solutions affords prima facie evidence of a gel-phase. This hypothesis, then, supposes that caoutchouc solutions of near 100 per cent. consist of little sol and much mechanically strong gel containing but little solvent; that very dilute solutions consist of relatively more sol and relatively little gel, the latter weak and highly distended; and that between the extremes there is a continuous gradation. Hence the viscosity, as measured by efflux, rises much more rapidly than the total concentration. At any given concentration there is a metastable equilibrium between the gel-phase and the sol-phase, the swelling tendencies of the former being counteracted by the true osmotic pressure of the latter. Spontaneous or accelerated ageing tends to shift the equilibrium in favour of the sol-phase.

Supposing, then, that a caoutchouc solution has part of its volume occupied by sol and the remainder by gel, the observed osmotic rises may be accounted for in two ways. Either, firstly, the gel-phase is osmotically inoperative, and the rise depends solely on the concentration of the sol-phase. If that were so, it would follow that as the total concentration rises the sol-phase becomes more concentrated than the gel-phase, and that as the viscosity of a given solution decreases the sol-phase becomes more dilute. Or, secondly, so much of the gel-phase as is in contact with the

diaphragm (corresponding with the ratio of gel-volume to sol-volume in the liquid) exerts simultaneously a pressure of the same character as that which causes caoutchouc, gelatin, etc., to swell when immersed in solvents, the observed rise being then a composite one. One would then expect the pressure developed inside a semi-permeable diaphragm to reach many atmospheres as the solution approached 100 per cent.; and, indeed, the pressures capable of being exerted by swelling colloids are well known to be of no mean magnitude. Which alternative is the more probable is not easy to decide in the present state of knowledge.

To the question of the molecular weight of dissolved caoutchouc the osmotic rises give no very definite answer. The van't Hoff relation can be applied only to the sol-phase, and postulates that the concentration of that phase be known; but with the diluted solutions, in which the gel-phase may be assumed to have almost disappeared, the measurement of osmotic pressure becomes very uncertain. From the data in tables I—V, a convergence of the molecular-weight value towards 100,000 is indicated in benzene and light petroleum solutions. The molecular weight of gutta-percha in benzene solution appears to be considerably smaller, since 40,000 is the limit towards which the values shown in table VII converge.

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## Organic Chemistry.

**Synthetic Preparation of Coal-gas.** LÉO VIGNON (*Bull. Soc. chim.*, 1914, [iv], 15, 601—604).—A gas similar to coal-gas can be prepared from water-gas by heating with lime and steam at  $400^{\circ}$ ; from a mixture of coke and lime in the presence of steam at  $600-1000^{\circ}$ , in accordance with the equation:  $4C + 6H_2O = 3CO_2 + 4H_2 + CH_4$ ; and from coal and lime at  $900-950^{\circ}$ . The method of preparation from coal yields 8 to 10 times the volume of gas obtainable by distillation, and converts most of the nitrogen of the coal into ammonia. The gas can also be prepared free from carbon monoxide, and non-toxic.

A. J. W.

**Preparation of Hexatriacontane.** A. OSKERKO (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 416—417).—*Hexatriacontane*,  $C_{36}H_{74}$ , was obtained as a secondary product in the synthesis of nonadecic acid from octadecyl bromide and magnesium (compare this vol., i, 921):  $C_{18}H_{37}Br + Mg = C_{36}H_{74} + MgBr_2$ . It forms large, white scales with a satiny lustre, m. p.  $76.5^{\circ}$ ,  $D_4^{20}$  0.764, cannot be distilled without decomposing, and has the normal molecular weight in boiling ethyl acetate.

T. H. P.

**Manufacture of Unsaturated Hydrocarbons.** WILLIAM HENRY EKKIN, FRANCIS EDWARD MATTHEWS, EDWARD HALFORD STRANGE, and LESBY JAMES WHEELER BLISS (Brit. Patent, 29988).—Doubly unsaturated hydrocarbons may be obtained by heating amino-alcohols with or passing them over catalysts such as phosphoric acid; for example,  $NH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH = CH_2 \cdot CH \cdot CH \cdot CH_2 + NH_3 + H_2O$ . The admixture of a diluent, such as steam, with the vapour of the amino-alcohol or the conduction of the process in a vacuum hinders secondary decomposition of the product, and the action of a substance like hydrogen chloride on the amino-alcohol may be employed as an intermediate step.

T. H. P.

**Preparation of Trimethylethylene [ $\beta$ -Methyl- $\Delta^2$ -butylene]** and of *iso*Amyl Alcohols from  $\beta$ -Methylbutane. CHEMISCHE FABRIK AUF AKTIEN (FORM. E. SCHERRING) (Austrian Patent, 63819).—The mixture of four *iso*amyl chlorides, b. p.  $85-105^{\circ}$ , obtained by chlorinating  $\beta$ -methylbutane, is treated with agents such as potassium acetate or alkali hydroxides which remove hydrogen chloride, and the resulting  $\beta$ -methyl- $\Delta^2$ -butylene distilled. The products of this reaction may be separated by distillation into a fraction boiling at a low temperature and containing the  $\beta$ -methyl- $\Delta^2$ -butylene, and one boiling at a higher temperature and containing the *iso*amyl alcohols or their esters.

T. H. P.

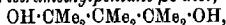
**The Physical Constants of Isoprene.** C. HARRIES (*Ber.*, 1914, 7, 1999—2003).—As there appears to be slight discrepancies between the recorded physical constants of isoprene (compare Steimmig, this vol. cvii. i.

vol., i, 560; Harries A., 1911, i, 798), the author has submitted samples of isoprene from two different sources to careful fractionation with the exclusion of air, and from his examination of the products arrives at the values b. p. 33.75—34.0°/762 mm,  $D_4^{16.5}$  0.6867,  $n_D^{16.5}$  1.42617 as the most probable for this substance. D. F. T.

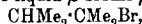
**Action of Metal-Ammoniums on the Halogen Derivatives of Methane Hydrocarbons. Application to the Estimation of the Halogens in Organic Compounds.** E. CHARLAV (*Ann. Chim.*, 1914, [ix], 1, 469—519).—A résumé of work already published (compare A., 1905, i, 502; 1906, i, 130, 722; 1907, i, 53, ii, 195; 1911, i, 939; 1912, i, 3, 244, 528; 1913, i, 241, 438). W. G.

**Investigation of the Grignard-Valeur Reaction for the Preparation of Glycols from Completely Substituted Ethyl Malonate and Organo-magnesium Iodides.** A. KALISCHY (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 427—453).—In spite of the statements of Valeur (A., 1901, i, 317; 1903, i, 416) and Dilthey and Last (A., 1904, i, 667), the author finds that not all esters of dibasic acids react completely with organo-magnesium compounds.

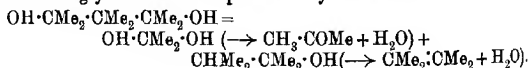
The interaction of ethyl dimethylmalonate and magnesium methyl iodide and subsequent decomposition by means of water of the product obtained yield (1) principally ethyl  $\beta$ -hydroxy- $\alpha\alpha$ - $\beta$ -trimethylbutyrate,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , which decomposes into ethyl isobutyrate and acetone, and (2)  $\beta\gamma\gamma\delta$ -tetramethylpentane- $\beta\delta$ -diol,



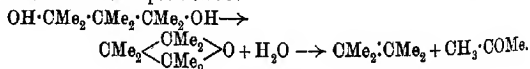
which forms feathery crystals, m. p. 75—76°, b. p. 233.5—234.5°/755 mm., and has the normal molecular weight in boiling ether. When heated with dilute sulphuric acid (1:10) or crystalline oxalic acid, the glycol yields  $\beta\gamma$ -dimethyl- $\Delta^2$ -butylene (tetramethylethylene), acetone, and water; a similar decomposition takes place initially when the glycol is treated (1) with red phosphorus and bromine, which give  $\beta\gamma$ -dibromo- $\beta\gamma$ -dimethylbutane,  $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$ , m. p. 169.5—170.5°, or (2) with hydrobromic acid saturated at 0°, which gives  $\beta\gamma$ -dibromo- $\beta\gamma$ -dimethylbutane and the liquid  $\beta$ -bromo- $\beta\gamma$ -dimethylbutane,



treatment of the latter with cold water giving dimethylisopropylcarbinol. According to Slavjanov (A., 1907, i, 578), the decomposition of the glycol would be represented by the scheme:



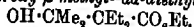
Since, however, no trace of the intermediate monohydric alcohol could be detected among the products of the action of either dilute sulphuric acid (1:10) or 5% acetic acid on the glycol, the author regards the course of the decomposition as:



In order to determine the influence of different radicals in com-

pletely substituted malonic esters on the reactivity of the two carboethoxy-groups, the following attempts to synthesise glycols have been carried out.

Ethyl diethylmalonate and magnesium methyl iodide yield no glycol, but only *ethyl β-hydroxy-β-methyl-αα-diethylbutyrate*,



b. p. 102–104°/8 mm.,  $D_4^{20}$  0.9696,  $n_D^{20}$  1.4450, and its decomposition products, acetone and ethyl α-ethylbutyrate, which, together with traces of β-hydroxy-β-methyl-αα-diethylbutyric acid, are obtained on treating the hydroxy-ester with 10% barium hydroxide solution at the ordinary temperature. Thus, in this case only one of the two carboethoxy-groups reacts with the magnesium methyl iodide.

Similarly, ethyl dipropylmalonate and magnesium methyl iodide yield no glycol, the product being ethyl β-hydroxy-β-methyl-αα-dipropylbutyrate, which gives acetone and ethyl α-propylvalerate on hydrolysis.

Ethyl dimethylmalonate and magnesium ethyl iodide yield ethyl β-hydroxy-αα-dimethyl-β-ethylvalerate, which decomposes on distillation under reduced pressure, and gives diethyl ketone and ethyl isobutyrate on hydrolysis.

Ethyl dimethylmalonate and magnesium propyl iodide give ethyl β-hydroxy-αα-dimethyl-β-propylhexoate, which decomposes into dipropyl ketone and ethyl isobutyrate. The corresponding acid,  $\text{OH} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , decomposes without melting at 175°.

Ethyl dimethylmalonate and magnesium phenyl iodide yield ethyl β-hydroxy-β-β-diphenyl-αα-dimethylpropionate, which decomposes into benzophenone and ethyl isobutyrate, and diphenyl, the latter resulting from the action of magnesium on iodobenzene.

In order to ascertain how the second carboethoxy-group of a completely substituted ethyl malonate behaves towards magnesium alkyl haloid after the first carboethoxy-group has been already substituted, a mixture of dipropyl ketone and ethyl α-bromoisobutyrate was treated with zinc. The resultant compound,  $\text{ZnBr} \cdot \text{O} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$ , was found to be unacted on by magnesium ethyl iodide, decomposition by means of water giving ethyl β-hydroxy-αα-dimethyl-β-propylhexoate, which yields dipropyl ketone and ethyl isobutyrate on hydrolysis.

The following general conclusions are drawn. The reaction,  $\text{CR}^1\text{R}^2(\text{CO}_2\text{Et})_2 + 4\text{MgR}^3\text{I}$ , proceeds completely only when  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  represent methyl groups. When one of these three methyl groups is replaced by another radicle, the second carboethoxy-group of the malonic ester loses its power to react with the magnesium alkyl haloid, so that the resulting compound is the ester of a hydroxy-acid. When one of the three radicles is hydrogen, the hydroxy-acid retains its tendency to rearrangement and rupture of the carbon skeleton; the smaller the radicles, the more stable is this skeleton. The reactions considered above afford a good method for obtaining symmetrical ketones.

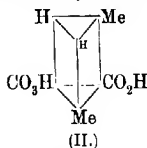
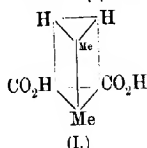
T. H. P.

**Preparation of Ethyl Sulphate.** LEON LILIENTHAL (Austrian Patent, 63526).—Ethyl sulphate may be obtained in 83–90% yield by distilling sodium ethyl sulphate in a vacuum.

T. H. P.

**Preparation of Aluminium Acetate Compounds Soluble in Water even after Evaporation.** KALLE & Co. ARTIEN-GESELLSCHAFT (D.R.-P. 272516).—When aluminium acetate solutions are treated with hexamethylenetetramine, with or without addition of a compound such as glycerol, mannitol, citric, lactic or tartaric acid, which increases the solubility of the aluminium acetate in water, evaporation of the liquids under diminished pressure results in the deposition of double compounds of hexamethylenetetramine and aluminium acetate. These double compounds are of more pleasant and less pronounced taste than aluminium acetate itself, and exhibit the therapeutic activity of the latter, together with the antiseptic action of the hexamethylenetetramine. T. H. F.

**Asymmetric Synthesis of *l*- and *d*- $\alpha$ -Methylbutyric Acids by means of Asymmetric Induction.** EMIL ERLKENMEYER [with F. LANDSBERGER] (*Biochem. Zeitsch.*, 1914, 64, 366—381).—The author develops his conceptions as to relative asymmetry in the case of methylethylmalonic acid. Marckwald has shown that an optically active  $\alpha$ -methylbutyric acid can be obtained by decomposing the acid brucine salt of this dibasic acid. It is supposed by the author that the symmetric form (I) can be converted into the asymmetric form (II).



The two forms on heating will decompose at different rates; and the formation of optically active  $\alpha$ -methylbutyric acid is not due in Marckwald's experiments merely to the fact that the crystalline salt employed contained more of the one antipode of the acid brucine salt than of the other, as, according to the theory, two acid brucine salts of the acid should exist. Experiments lead to the conclusion that the formation of the active  $\alpha$ -methylbutyric acid is due to asymmetric induction. In the first place an active  $\alpha$ -methylbutyric acid was obtained from the acid brucine salt by adding the brucine (in theoretical quantity) to an alcoholic solution of methylethylmalonic acid, and evaporating off the solvent entirely. Under such conditions, no separation of fractions of a brucine salt could take place. In the second place it was shown that *l*- $\alpha$ -methylbutyric acid could be obtained by heating methylethylmalonic acid with one equivalent of *d*-tartaric acid and *d*- $\alpha$ -methylbutyric acid could be obtained in a corresponding manner when *l*-tartaric acid was employed. S. B. S.

**Preparation of Hexamethylenetetramine Salts of Palmitic and Stearic Acids.** PHILIPP RÖDER-BRUNO RAABE ARTIENGESELLSCHAFT and ARTHUR WÖBER (Austrian Patent, 63822).—These salts are prepared by heating the molten acid (1 mol.) with the base (1 mol. either solid or dissolved in water or aqueous alcohol. Both are readily soluble in hot water, giving neutral solutions.

*Hexamethylenetetramine stearate*,  $C_6H_{12}N_4C_{17}H_{35}\cdot CO_2H$ , forms a stable, microcrystalline powder, decomposing at about  $140^\circ$  with liberation of formaldehyde and ammonia.

*Hexamethylenetetramine palmitate*,  $C_6H_{12}N_4C_{15}H_{31}\cdot CO_2H$ , forms a stable, crystalline powder, decomposing at  $130-140^\circ$ , with liberation of formaldehyde and ammonia.

T. H. P.

**Preparation of  $\Delta^9$ -Nonadecenoic Acid.** A. OSKERKO (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 411—416).—Ethyl stearate was reduced by means of sodium to octadecyl alcohol, which was converted by heating with hydrobromic acid into octadecyl bromide, the latter being treated with magnesium and carbon dioxide to obtain nonadecenoic acid, and this heated with bromine and red phosphorus to transform it into  $\alpha$ -bromononadecenoic acid. Removal of hydrogen bromide under the influence of diethylaniline resulted in the formation of  $\Delta^9$ -nonadecenoic acid.

*Octadecyl bromide*,  $CH_3\cdot[CH_2]_{16}\cdot CH_2Br$ , crystallises from absolute alcohol in silvery-white scales, m. p.  $28.5^\circ$ .

*$\alpha$ -Bromononadecenoic acid*,  $CH_3\cdot[CH_2]_{16}\cdot CHBr\cdot CO_2H$ , crystallises from light petroleum in yellowish, and from alcohol in snow-white, plates, m. p.  $59-60^\circ$ .

*$\Delta^9$ -Nonadecenoic acid*,  $CH_3\cdot[CH_2]_{15}\cdot CH\cdot CH\cdot CO_2H$ , separates from alcohol or light petroleum in drusy masses of small, white crystals, m. p.  $51.5^\circ$ . It decolorises alkaline permanganate solution, and in chloroform solution rapidly combines with bromine in the cold, thus differing from  $\Delta^9$ -oleic acid (compare Le Sueur, T., 1904, 85, 1708; Ponzio, A., 1904, i, 548).

*$\alpha$ -Hydroxynonadecenoic acid*,  $CH_3\cdot[CH_2]_{16}\cdot CH(OH)\cdot CO_2H$ , forms white leaflets, m. p.  $83-84^\circ$ .

T. H. P.

**Naphthenic Acids of High Molecular Weight from Baku Petroleum.** EWALD PYHÄLÄ (*Zeitsch. angew. Chem.*, 1914, 27, 407).

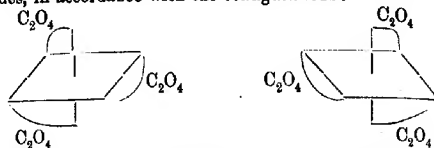
—By treatment of the alkaline machine oil residues from Baku petroleum with sulphuric acid, and subsequent purification of the precipitated oil by extraction with alcoholic potassium hydroxide and by distillation, a colourless, viscid oil, consisting of a mixture of naphthenic acids, was obtained. It possessed the following physical constants:  $D_{15}^{20}$  1.9470, acid value 168.7, iodine value 2.54. By fractional distillation 13% was obtained boiling at  $310-320^\circ$ , and 63% at about  $340^\circ$ . The lower fraction had an acid number 180.4, corresponding with a molecular weight of 310, and is therefore regarded as an *eicoenoic acid*,  $C_{19}H_{37}\cdot CO_2H$ , an assumption in accord with the composition of the silver salt. The higher fraction,  $D_{15}^{20}$  0.9400, had an acid number 47.6, corresponding with a molecular weight of 380. The analysis of the silver and barium salts showed it to be *eicosipentacosenoic acid*,  $C_{24}H_{47}\cdot CO_2H$ .

G. F. M.

**Mirror Image Isomerism with Rhodium Compounds. II.**  
A. WERNER [with J. POUPARDIN] (*Ber.*, 1914, 47, 1954—1960).—



The rhodium oxalates of the formula  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{M}_3$  should give optical isomerides, in accordance with the configurations:



The resolution of the potassium salt,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , was readily accomplished by means of strychnine nitrate. Fractional crystallisation gave the *d*-strychnine salt as the least soluble fraction, the *l*-salt being much more readily soluble. From the strychnine salts the potassium, sodium, rubidium, and barium salts were obtained by double decomposition with the respective iodides.

The rotatory power of the rhodium oxalates is less than that of the corresponding chromium oxalates, but whereas the latter undergo racemisation very readily in aqueous solution, the former are quite stable; their aqueous solutions can be warmed on the water-bath without appreciable change. The rotation-dispersion of the rhodium salts is very marked, the direction of rotation undergoing a change at the *D*-line, as shown by the following figures for the potassium salt,

$$[\alpha]_C - 26.4^\circ, [\alpha]_D 0^\circ, [\alpha]_E + 114.4^\circ.$$

It is noteworthy that all the metal oxalates which have been obtained as optically active isomerides, namely, those of chromium, rhodium and cobalt, show abnormal dispersion.

The active rhodium salts crystallise in well-developed, garnet-red crystals, which are more readily soluble than the racemic salts. The potassium salts can crystallise out together from the solution of the racemate and the isomerides be separated mechanically; the crystals show hemihedral faces and belong to the triclinic system. This is the first case of the resolution of inorganic compounds by spontaneous crystallisation.

*Strychnine d-rhodium oxalate*,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{H}_3\text{Stry} \cdot 2\text{H}_2\text{O}$ , in a 0.1% solution has  $[\alpha]_C^{18} - 30^\circ$ ,  $[\text{M}]_C^{18} - 421.74^\circ$ ,  $[\alpha]_D^{18} - 25^\circ$ ,  $[\text{M}]_D^{18} - 351.45^\circ$ ,  $[\alpha]_E^{18} + 14.5^\circ$ ,  $[\text{M}]_E^{18} + 203.8^\circ$ ,  $[\alpha]_F^{18} + 102.3^\circ$ ,  $[\text{M}]_F^{18} + 1438.1^\circ$ . The corresponding *l*-salt,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{H}_3\text{Stry} \cdot 9\text{H}_2\text{O}$ , has  $[\alpha]_C^{18} - 40^\circ$ ,  $[\text{M}]_C^{18} - 346.4^\circ$ ,  $[\alpha]_D^{18} - 165^\circ$ ,  $[\text{M}]_D^{18} - 1429^\circ$ ,  $[\alpha]_E^{18} - 75^\circ$ ,  $[\text{M}]_E^{18} - 619.5^\circ$ .

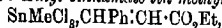
The *d*- and *l*-potassium rhodium oxalate,  $\text{K}_3\text{Y} \cdot \text{H}_2\text{O}$ , where  $\text{Y} = \text{Rh}(\text{C}_2\text{O}_4)_3$ , give well-developed, red, prismatic crystals. The former has  $[\alpha]_C^{18} - 26.4^\circ$ ,  $[\text{M}]_C^{18} - 132.53^\circ$ ,  $[\alpha]_D^{18} + 114.4^\circ$ ,  $[\text{M}]_D^{18} + 574.28^\circ$ , and the latter,  $[\alpha]_C^{18} + 30^\circ$ ,  $[\text{M}]_C^{18} + 150^\circ$ ,  $[\alpha]_D^{18} - 124^\circ$ ,  $[\text{M}]_D^{18} - 622^\circ$ , both in 0.5% solution. The *d*- and *l*-sodium rhodium oxalates,  $\text{Na}_3\text{Y} \cdot 4\text{H}_2\text{O}$ , have  $[\alpha]_C^{18} - 30^\circ$ ,  $[\text{M}]_C^{18} - 152^\circ$ , and  $[\alpha]_D^{18} + 38^\circ$ ,  $[\text{M}]_D^{18} + 142^\circ$ , both in 0.5% solution; they form orange-red, hygroscopic crystals. The *d*- and *l*-rubidium rhodium oxalates,  $\text{Rb}_3\text{Y} \cdot \text{H}_2\text{O}$ , form garnet-red, tetrahedral crystals, having respectively  $[\alpha]_C^{18} \mp 30^\circ$ ,  $[\text{M}]_C^{18} \mp 192^\circ$ , in 0.5% solution. The *d*- and *l*-barium salts,  $\text{Ba}_3\text{Y} \cdot 3$  or  $2\text{H}_2\text{O}$ , crystallise in efflorescent, red needles, and have  $[\alpha]_C^{18} \mp 24^\circ$ ,  $[\text{M}]_C^{18} \mp 275^\circ$ , in 0.5% solution. One gram of the anhydrous salt is soluble in 246 c.c. of water at  $18^\circ$ . T. S. P.

**The Variable Affinity of the Subsidiary Valencies of Tin.**  
P. PFIFFER and O. HALPERIN (*Zeitsch. anorg. Chem.*, 1914, 87, 335—352).—Stannic chloride has the greatest power of forming additive compounds of all the tin haloids as it combines with esters of carboxylic acids, in addition to ethers and similar compounds. The derivatives of stannic bromide are less stable, and it does not form solid compounds with all the esters examined. Stannic iodide and tin alkyl haloids have much less power of forming additive compounds, phenyl having a still greater effect than alkyl. The derivatives of dicarboxylic esters must be formulated as cyclic compounds.

*Di-ethyl carbonate tin tetrachloride*,  $\text{SnCl}_4 \cdot 2\text{CO}(\text{OEt})_2$ , forms highly hygroscopic, colourless leaflets, decomposed by water. The *ethyl malonate* compound,  $\text{SnCl}_4 \cdot \text{CH}_2(\text{CO}_2\text{Et})_2$ , has m. p. 115—117°, and a compound with 2 mols. of the ester has not been obtained. The compounds with *methyl succinate*,  $\text{SnCl}_4 \cdot \text{C}_4\text{H}_7(\text{CO}_2\text{Me})_2$ , and *ethyl succinate*,  $\text{SnCl}_4 \cdot \text{C}_4\text{H}_7(\text{CO}_2\text{Et})_2$ , melt at 138° and 95° respectively. *Ethyl glutarate* forms a compound  $\text{SnCl}_4 \cdot \text{CH}_2(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$ , and *ethyl phthalate* a compound,  $\text{SnCl}_4 \cdot \text{C}_8\text{H}_5(\text{CO}_2\text{Et})_2$ .

*Di-ethyl cinnamate tin tetrabromide*,  $\text{SnBr}_4 \cdot 2\text{CHPh}:\text{CH}_2 \cdot \text{CO}_2\text{Et}$ , has m. p. 70—72°; the compounds with ethyl carbonate, ethyl malonate (m. p. 63—65°), and ethyl succinate contain 2 mols. of the ester, and are very unstable. *Acetonitrile tin tetrabromide*,  $\text{SnBr}_4 \cdot 2\text{MeCN}$ , decomposes readily at the ordinary temperature. Ether and many dicarboxylic esters fail to form compounds. Tin tetraiodide crystallises unchanged from the esters, and also from ether and acetonitrile.

The alkyl derivatives combine in very few cases. The only compound obtained is: *Ethyl cinnamate tin methyl chloride*,

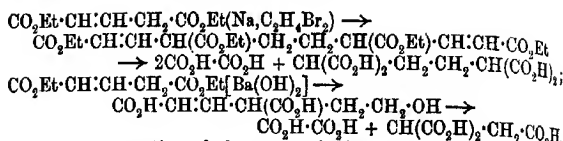


m. p. 50—55°.

C. H. D.

**Trimethyleneglutaric [αα-Ethyleneglutaric Acid].** B. K. МАРШКОВСКИ (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 517—526).—The author has repeated the work of Fecht (A., 1907, i, 906), who regarded (1) the acid, described as αα-ethyleneglutaric acid, obtained by hydrolysis of the nitrile formed from the dibromide of vinyltrimethylene as identical with (2) that prepared from ethyl glutaconate, ethylene dibromide and sodium ethoxide in alcoholic solution and drew the conclusion that vinyltrimethylene is actually *spiropentane*. Fecht, however, miscalculated the results of his analyses, his weighings showing that acid (1) contains 55.57% C and 6.63% H and not 53.05% C and 6.56% H, and acid (2) 52.78% C and 6.29% H and not 52.98% C and 6.26% H.

Further, an acid of the structure  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}:\text{CH} \cdot \text{CO}_2\text{H}$  should give, when oxidised with alkaline permanganate, oxalic and cyclopropane-1:1-dicarboxylic acids, whereas the author obtains oxalic, formic, ethanetricarboxylic (carboxysuccinic), and hexanedicarboxylic acids, together with a number of other products, but no cyclopropane-dicarboxylic acid. A more probable scheme for the condensation of ethyl sodioglutaconate and ethylene bromide and for subsequent hydrolysis and oxidation of the resultant product is as follows:



In the preparation of the ester of dicarboxysodiogluconic acid from ethyl sodiomalonate and chloroform according to the equation:  $4\text{CHNa}(\text{CO}_2\text{Et})_2 + \text{CHCl}_3 = \text{C}(\text{CO}_2\text{Et})_2\cdot\text{CNa}\cdot\text{CH}(\text{CO}_2\text{Et})_3 + 3\text{NaCl} + 2\text{CH}_2(\text{CO}_2\text{Et})_2$ , yields of 86, 152, and 176 grams were obtained instead of the theoretical quantities, 70.4, 131 and 141.6 grams, whereas the ethyl malonate also formed amounted to only 20% instead of 50% of the original quantity. It seems probable that further condensation occurs between the tetracarboxylic ester and the malonic esters.

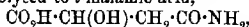
The conclusion is drawn that the acid examined by Fecht was not *aa*-ethyleneglutaric acid, but a complex mixture of condensation products.

T. H. P.

**Preparation of an Acid Calcium Lactate.** CHEMISCHES WERKE VORM. HEINRICH BYK (D.R.-P. 271643).—A calcium hydrogen lactate containing three lactic acid residues per atom of calcium may be obtained (1) by treating the ordinary acid salt composed of 1 mol. of calcium lactate and 1 mol. of lactic acid with a solvent, such as cold alcohol, for lactic acid, or (2) by evaporating calcium oxide, hydroxide, carbonate or lactate with sufficient or more than sufficient lactic acid to give 3 mols. of the acid per atom of calcium, any excess of acid being subsequently removed by means of a solvent. The salt is readily soluble in water, and its free lactic acid is more stably held than the second molecule of acid in the ordinary acid lactate.

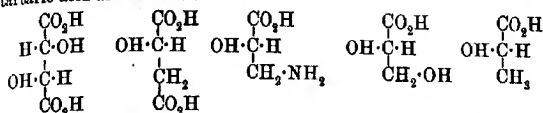
T. H. P.

**The Configuration of the Glyceric and Lactic Acids.** KARL FREUDENBERG (*Ber.*, 1914, 47, 2027–2037).—The configuration of *d*-tartaric acid as derived from that of dextrose (Fischer, A., 1896, i, 525) should also decide that of the malic acids, for the reduction of *d*-tartaric acid gives *d*-malic acid, although in poor yield. On treatment with barium hydroxide solution at 60°, the amide of *l*-malic acid is hydrolysed to *l*-malamic acid,



which is smoothly converted by barium hydroxide solution and bromine into *l*-isoserine,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ . This substance, under the action of nitrous acid, gives *d*-glyceric acid (compare Fischer and Jacobs, A., 1907, i, 393), the yield being 22% of the theoretical. When treated in hydrobromic acid solution with nitric acid and bromine, *l*-isoserine undergoes conversion into *d*- $\beta$ -bromolactic acid, m. p. 80°,  $[\alpha]_D^{20} + 2.01^\circ$  (in aqueous solution), which can also be obtained by resolution of the synthetic racemic acid with morphine. Reduction with sodium amalgam and dilute sulphuric acid at 15–20° converts *d*-bromolactic acid into *d*-lactic acid (zinc salt,  $[\alpha]_D^{17} - 7.44^\circ$  in water).

From these results the following structures are deduced, taking *d*-tartaric acid as standard:



*d*-Tartaric acid. *l*-Malic acid. *l*-isoSerine. *d*-Glyceric acid. *d*-Lactic acid.

These configurations agree with those indicated by the action of *Penicillium glaucum* on the various racemic acids (Mackenzie and Harden, T., 1903, 83, 424; compare, however, Neuberg and Silbermann, A., 1907, i, 408).

D. F. T.

**Behaviour of Crotonic Acid in Ultra-violet Light.** I. R. STOERMER and H. STOCKMANN (*Ber.*, 1914, 47, 1786—1793).—The only exceptions which Stoermer has yet encountered, to the rule that the simple ethylenic acids are transformed into labile varieties under the influence of ultra-violet light, are crotonic and mesaconic acids. The former acid has again been examined but with no better result, which is remarkable, since the amide is transformed into *isocrotonamide* to an unusually great extent. When crotonic acid is illuminated in other than indifferent solvents, however, addition of the medium takes place, according to the common rule that the active hydrogen atom enters the  $\alpha$ -position, and the remaining radicle, the  $\beta$ -position.

One of the difficulties in deciding whether crotonic acid is transformed into *isocrotonic* acid at all, is to separate a trace of the labile acid from the unchanged material. The few methods which have been proposed have been tried and found to be unsatisfactory. In one case, the product, after illuminating 100 grams of crotonic acid in benzene solution before a Uviol lamp for five weeks, was converted into the sodium salt, only 1.2 grams of which dissolved readily in absolute alcohol. The dry salt was suspended in ether, treated with thionyl chloride, and then with aniline, but it was impossible to isolate an anilide with the m. p. of pure *isocrotonanilide*.

The amides have now been prepared in a pure state, and these differ sufficiently in solubility. An ethereal solution of crotonyl chloride, prepared as above, was strongly cooled and slowly added to liquid ammonia, and the dry residue left on evaporation was recrystallised from acetone. *Crotonamide*,  $\text{CH}_3\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , forms glistening, white needles, m. p. 159.5—160°, which are more soluble in water than in organic media. The amide was dissolved in acetone, and exposed to the Uviol lamp for three weeks, when the residue was extracted with hot benzene. The unchanged amide crystallised at once and was filtered, when *isocrotonamide* separated in slender leaflets, m. p. 102°, the transformation having taken place to the extent of 11.6%.

An aqueous solution of sodium crotonate was illuminated for six weeks, when the dried salt was extracted with alcohol. A yield of 24% of sodium  $\beta$ -hydroxybutyrate was obtained from the extract. Free crotonic acid does not so readily combine with water, the yield of

$\beta$ -hydroxybutyric acid being only 10%. The insolubility of sodium crotonate was also made use of in separating the products obtained in methyl or ethyl alcohol. Slightly less than a 10% yield of  $\beta$ -methoxybutyric acid, b. p. 117–118°/20 mm., 212–214°/atm., was obtained in the one case, and a 6.8% yield of  $\beta$ -ethoxybutyric acid, b. p. 113°/14 mm., in the other.

J. C. W.

**Does Osmium Dioxide Act as a Catalyst in Hardening Fats?**  
W. NORMANN and F. SCHICK (*Arch. Pharm.*, 1914, 252, 208–210).—When osmium tetroxide (which is a non-conductor) is heated with oleic acid, the undissolved residue, after being freed from the blackened oil and washed with petroleum, is a good conductor of electricity. The tetroxide under these conditions, therefore, is not converted into osmium dioxide, as Lehmann states (*A.*, 1913, ii, 331), but is reduced to the metal. In this case, therefore, as also in those of the oxides of copper and nickel (Meigen and Bartels, this vol., i, 482), the catalyst in the hydrogenation of fats is the metal, not the oxide.

C. S.

**Determination of the Constitution of Enols.** JOHANNES SCHEIBER and PAUL HEROLD (*Annalen*, 1914, 405, 295–346).—According to Claisen's rule a substance containing the group  $R \cdot CO \cdot \dot{C}H \cdot COR'$  enolises to  $OH \cdot CR \cdot \dot{C} \cdot COR'$  if  $-COR$  is the more negative acyl group, for example, benzoylacetone enolises to  $OH \cdot CMc \cdot CHBz$ .

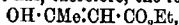
His titration method leads Meyer to the opposite opinion, the enol having the formula  $CHAc \cdot CPh \cdot OH$ , since the enolisation tendency of the benzoyl group is greater than that of the acetyl (*A.*, 1912, i, 940). The authors have made a comprehensive survey of the numerous physical and chemical methods which have been employed to determine the constitution of enols, and are of opinion that a generally applicable process has not yet been brought forward. They have applied the ozonide method to the solution of the problem (*A.*, 1913, i, 490) and claim for it the following advantages. Enols rapidly unite additively with ozone at  $-20^\circ$ , therefore under conditions which prevent or render improbable any transformation of the primarily existent complex into a more reactive form. Desmotropic ketonic modifications do not react with ozone, whilst the corresponding enols do. Keto-enolic transformations are not catalytically influenced by ozone, because partly enolised substances are only partly converted into ozonides.

The method of working is as follows. A solution of 1–2 grams of the substance in dry chloroform or carbon tetrachloride is cooled to  $-20^\circ$  with careful exclusion of moisture, and is then treated with 6–8% unwashed ozone until a persistent odour of the latter is observed. The time required may be only a few moments, but usually two to three hours is sufficient. The solvent is removed by a current of dry air at  $0^\circ$ , and the residue is treated with water at the ordinary temperature. The decomposition of the ozonide proceeds vigorously, but not explosively. The fission products are always kept in contact with the water overnight before being examined.

Ethyl malonate is quite stable to ozone, and does not yield a trace

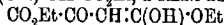
of carbon dioxide or of ethyl glyoxalate; its formula, therefore, is  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , a result in agreement with that of Meyer's volumetric process.

Even after many hours' treatment, ethyl acetoacetate yields only a small quantity of an ozonide, the decomposition products of which contain acetic acid and ethyl glyoxylate (*loc. cit.*), but not carbon dioxide, methylglyoxal, or alcohol. The enol present in ethyl acetoacetate in small amount has, therefore, the formula



not  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{OEt}$  (compare Bielecki and Henri, this vol., ii, 318).

Ethyl oxalacetate is easily and completely converted into an ozonide, the decomposition products of which contain oxalic acid, ethyl glyoxylate (identified as the phenylhydrazone, m. p. 128°), and a small quantity of carbon dioxide. The predominating enol, therefore, has the formula  $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , a small amount of



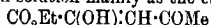
also being present (compare Meyer, *loc. cit.*).

Ethyl benzoylacetate is only partly converted into an ozonide the decomposition of which yields benzoic acid and ethyl glyoxylate, but not carbon dioxide. The enol, therefore, is  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ .

Acetylacetone is incompletely but easily ozonised. The decomposition products contain methylglyoxal (osazone, m. p. 146°) and carbon dioxide. The enolised portion of the diketone is, therefore, partly the enol,  $\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CMe}$ , and partly the dienol,  $\text{CMe}(\text{OH})\cdot\text{C}\cdot\text{CMe}\cdot\text{OH}$  (see below).

The results previously recorded in connexion with benzoylacetone (*loc. cit.*) require correction. The ozonide is obtained quantitatively, and gives by its decomposition an almost quantitative yield of benzoic acid, methylglyoxal (the directly precipitated osazone has m. p. 135–140°, instead of 146°, and therefore contains an impurity, probably phenylglyoxalosazone), and carbon dioxide. Benzoylacetone exists in solution, therefore, mainly as the enol  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CMe}$ ; the other enol,  $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COPh}$ , and the dienol,  $\text{OH}\cdot\text{CPh}\cdot\text{C}\cdot\text{CMe}\cdot\text{OH}$ , are also present in small amount.

Oxalacetone exists in solution mainly as the enol



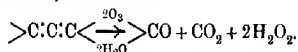
and to a small extent as the enol  $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  (*loc. cit.*); in addition, a considerable amount of the dienol must be present because the decomposition of the ozonide yields a considerable quantity of carbon dioxide, and, moreover, Meyer's volumetric process gives results indicating far more than 100% of enol.

Oxalacetophenone exhibits remarkable behaviour. It is only slightly attacked by ozone even although Meyer's method shows the presence of at least 100% of enol. The decomposition products of the ozonide are benzoic and oxalic acids, phenylglyoxal and ethyl glyoxyl-formate (both identified as the osazones), and carbon dioxide. The first four of these products are those which would be expected from the decomposition of the two enols  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}\cdot\text{CPh}\cdot\text{OH}$  and  $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COPh}$ . Oxalacetophenone, however, cannot consist of these two enols because there is no reason why they should not

form ozonides. The production of carbon dioxide during the decomposition of the ozonide indicates that a dienol is present, but a satisfactory explanation of the behaviour of oxaloacetophenone cannot yet be given. Dibenzoylmethane is another substance which is scarcely attacked by ozone at 0°, although the volumetric method indicates the presence of about 100% of enol.

The ketonic modification, m. p. 108—110°, of dibenzoylacetylmethane is unattacked by ozone, but the enol, m. p. 80—85°, yields a yellow ozonide by the decomposition of which are produced benzoic acid and the hydrate, m. p. 55—60°, of phenyl methyl triketone (identified as the semicarbazone, m. p. 190°, and phenylhydrazone, m. p. 165°). The formation of these two substances indicates that the enol of dibenzoylacetylmethane is mainly  $\text{OH}\cdot\text{CPh}:\text{C}(\text{COMe})\cdot\text{COPh}$ , but the presence of a small amount of the other enol,  $\text{OH}\cdot\text{CMe}:\text{C}(\text{COPh})_2$ , is possible even although acetic acid and diphenyl triketone could not be detected among the products of decomposition of the ozonide.

The presence of carbon dioxide amongst the decomposition products of the ozonides of diacetylmanes indicates the presence of accumulated double linkings, that is, of dienols:



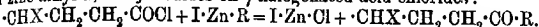
The estimation of carbon dioxide produced by the decomposition of an ozonide is not easy, but a gravimetric apparatus is described which gives quite satisfactory results, the absorption vessel gaining only about 2 mg. in weight when the ozonide of a substance which cannot contain accumulated double linkings is decomposed. The following generalisations are deduced from the amounts of carbon dioxide produced during the decomposition of the ozonides of the substances mentioned above. The groups  $\cdot\text{CO}_2\text{Et}$ ,  $\cdot\text{COMe}$ ,  $\cdot\text{COPh}$ , and  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  tend to enolise in the order given; the carbethoxy has little or no tendency, whilst  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  has a very great tendency. A group which has little tendency to enolise may be induced to do so by the presence of a pronouncedly enolisable group; thus, ethyl acetoacetate does not form any dienol, whereas ethyl oxalacetate does to a slight extent, the carbethoxy-group enolising in the presence of the  $\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  group.

The  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modifications of ethyl formylphenylacetate (Wislicenus, A., 1912, i, 623) each form an ozonide by the decomposition of which are produced formic acid and ethyl phenylglyoxylate (identified as the phenylhydrazone), together with a little carbon dioxide, formed, probably, by the ozonisation of performic acid (d'Ans and Frey, A., 1912, i, 601). The enol in the  $\alpha$ -ester and the  $\gamma$ -ester, therefore, are stereoisomeric oxymethylenes, not structural isomerides as Wislicenus is inclined to believe (*loc. cit.*; compare also Meyer, A., 1912, i, 861).

The authors have also examined the enolic modifications of ethyl diacetylsuccinate (Knorr, A., 1899, i, 673). The  $\alpha_2$ -ester, m. p. 31—32°, does not form an ozonide. The  $\alpha_1$ -ester yields an ozonide the decomposition products of which are oxalic acid, ethyl diketobutyrate, and probably formaldehyde. The  $\alpha_4$ -ester (prepared from the di-sodio-

derivative) forms an ozonide which yields oxalic and acetic acids, formaldehyde, and ethyl diketobutyrate, but not ethyl diketosuccinate. The authors interpret these results to denote that (i) the  $\alpha_2$ -ester is ketonic, not enolic; they show that it does not react with alcoholic bromine; (ii) the  $\alpha_1$ -ester is a mixture of an enolic and a ketonic (probably  $\alpha_2$ ) modification. Meyer's volumetric method indicates that there is also present an enol which does not react with bromine, but does form an ozonide; (iii) the  $\alpha_1$ -ester is also a mixture of an enolic and a ketonic modification. C. S.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc.  $\gamma$ -Chloroketones and Corresponding Products of Hydrolysis. HENRI WOHLGEMUTH (*Compt. rend.*, 1914, 159, 80—82).— $\gamma$ -Halogenated ketones can be readily prepared by the action of zinc alkyl and aryl iodides on  $\gamma$ -halogenated acid chlorides:



A number of such ketones have been prepared from  $\gamma$ -chlorobutyl chloride,  $\gamma$ -chloro-*n*-valeryl chloride and  $\gamma$ -bromo-*n*-valeryl chloride. The condensation of these acid chlorides with zinc ethyl iodide at 0° only gives a small yield of the required ketone, the main products being tarry, resulting from a more advanced condensation, amongst which esters of tertiary  $\gamma$ -chloro-alcohols have been isolated. The author has prepared  $\delta$ -chloro- $\alpha\alpha$ -diethylbutyl  $\gamma$ -chlorobutyrate,  $\text{CH}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CET}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , b. p. 172—174°/17 mm. Good yields of the required ketones are, however, obtained by effecting the condensation at -15° to -20°, and the following compounds are described: ethyl  $\gamma$ -chloro-*n*-butyl ketone, b. p. 79°/13 mm., giving a semicarbazone, m. p. 129—129.5°; ethyl  $\gamma$ -chloropropyl ketone, b. p. 80—80.5°/17 mm., giving a semicarbazone, m. p. 118°, and a *p*-nitrophenylhydrazone, m. p. 106—107°; ethyl  $\gamma$ -bromo-*n*-butyl ketone, b. p. 88—89°/11 mm., giving a semicarbazone, m. p. 142° (decomp.); phenyl  $\gamma$ -chloro-*n*-butyl ketone, b. p. 155—156°/15 mm., giving a semicarbazone, m. p. 123°; and *p*-tolyl  $\gamma$ -chloropropyl ketone, white leaflets, m. p. 33.5°, giving a semicarbazone, m. p. 186°.

These  $\gamma$ -chloro-acyclic ketones are easily hydrolysed by boiling with water, giving the corresponding  $\gamma$ -hydroxyketones which readily undergo dehydration, giving  $\alpha$ - and  $\beta$ -dihydrofuran derivatives, these latter being obtained by distilling the  $\gamma$ -hydroxyketones under atmospheric pressure. Thus ethyl  $\gamma$ -hydroxy-*n*-butyl ketone, a colourless, oily liquid, b. p. 86.5°/11 mm., gives an anhydride, b. p. 122—123°, a semicarbazone, m. p. 91°, and a phenylurethane, m. p. 79°.

Ethyl  $\gamma$ -hydroxypropyl ketone, b. p. 115—116°/21 mm., gives an anhydride, b. p. 109—110°, and a phenylurethane, m. p. 84°.

On reduction with sodium amalgam the  $\gamma$ -hydroxyketones readily yield the corresponding  $\gamma$ -glycols, colourless oils, which, on boiling with 33% aqueous sulphuric acid, yield quantitatively alkyltetrahydrofurans. Thus hexane- $\alpha\delta$ -diol, b. p. 134—135°/18.5 mm., yields a diacetate, a mobile liquid, b. p. 122°/14 mm., a diphenylurethane, m. p. 82°, and 2-ethyltetrahydrofuran, b. p. 107—108°/770 mm.

Heptane- $\beta\epsilon$ -diol, b. p. 132°/18.4 mm., yields a diphenylurethane, m. p. 147°, and 2-methyl-5-ethyltetrahydrofuran, b. p. 117—118°.



Methyl  $\gamma$ -hydroxypropyl ketone reacts in the cold in alcohol with phenylhydrazine to give a cyclic compound (compare Lipp, A., 1889, 843), and its oxime at  $100^{\circ}$  loses water and gives a cyclic compound (compare Marshall and Perkin, T., 1891, 59, 880).

Ethyl  $\gamma$ -hydroxy-*n*-butyl ketone, on the other hand, yields a normal phenylhydrazone, an oil, and an oxime, a colourless oil, b. p.  $149-150^{\circ}/13$  mm., without change. The  $\gamma$ -chloro-ketones, however, readily yield cyclic compounds. W. G.

Plant Colloids. IV. Displacement of the Phosphorus Content by Changes of Condition and the Diastatic Decomposition of Starch. MAX SAMEC (*Koll. Chem. Beihefte*, 1914, 6, 23-54. Compare A., 1913, i, 17, 1155).—By the action of 0.125*N*. potassium hydroxide on a starch suspension, it has been found possible to separate the starch into two fractions, one of which contains phosphoric acid, whilst the other is practically free. The products were purified by prolonged dialysis, and as a result, 38 grams of phosphorus-free amylose and 49 grams of amylopectin were obtained. The aqueous solutions of amylose are non-conducting, and their viscosity is not affected by the addition of acid or alkali. The readiness with which the amylose is coagulated by alcohol is, however, as in the case of the original starch, increased by acids and diminished by alkalis. These observations show clearly that the physico-chemical properties of starch solutions are to a considerable extent determined by the phosphorus content.

Since it is probable that the high viscosity of starch solutions is determined by the amylopectin, and since this is decomposed by the action of diastase, it was to be expected that diastatic decomposition of starch would lead to the liberation of the inorganic substance. The experiments which have been made in this connexion confirm this view, for it has been found that dextrans containing phosphorus are formed in the action of diastase on starch and that these compounds exhibit the properties of electronegative colloids. By the action of boiling water, phosphoric acid is set free from the products of the diastatic action. H. M. D.

The Action of Ultra-violet Rays on Lævulose. The Formation of Formaldehyde and Carbon Monoxide. ALBERT RANC (*Biochem. Zeitsch.*, 1914, 64, 257-287; *Bull. Soc. chim. Biol.*, 1914, 1, 26-36).—Under the action of ultra-violet rays, lævulose in solution undergoes scission with the formation of formaldehyde, carbon monoxide, carbon dioxide, methyl alcohol, and substances of aldehydic and acid character, which have not been further identified. It is claimed that the degradation of this sugar has been produced for the first time without the agency of either chemicals or ferments.

S. B. S.

Inversion of Sucrose Solution by Aspartic Acid. LEOPOLD RADLBERGER and WILHELM SIEGMUND (*Chem. Zentr.*, 1914, i, 1556-1557; from *Österr.-ung. Zeitsch. Zucker-Ind. Landw.*, 43, 29-43).—Experiments on the inversion of sucrose by inactive

aspartic acid have been carried out at temperatures from 30° to 80° with an interval of 5°. The periods were 0, 5, 10, 15, 30, 60, 120, 180, and 240 minutes. At the end of each experiment, the solution was immediately rendered alkaline with sodium hydroxide, cooled to 20°, and the invert-sugar estimated by Herzfeld's method. The results are given in a series of tables and curves. The increase in the formation of invert-sugar during equal intervals with increasing temperature, and also with increasing periods, can be represented by fairly regular curves which rise more rapidly at higher than at lower temperatures.

H. W.

**Lactal and Hydrolactal.** EMIL FISCHER and GEORGE O. CURME, jun. (*Ber.*, 1914, 47, 2047—2057).—In a recent paper on the reduction of acetobromoglucose to triacetylglucal and the hydrolysis of the latter to glucal, it was briefly stated that acetobromolactose behaved similarly (this vol., i, 253). A complete account of "acetolactal," or more strictly speaking, hexa-acetyl-lactal and of lactal and hydrolactal is now given. The relationship between these compounds and lactose is demonstrated by the production of mucic acid on oxidation. The formation of hydroglucal, by the action of emulsin on hydrolactal, also shows that it is the dextrose part of the lactose molecule which is affected by the above reduction.

Acetobromolactose, prepared by the action of hydrogen bromide and glacial acetic acid on octa-acetyl-lactose, was shaken with zinc dust and 50% acetic acid at 0°, until the sugar completely dissolved. The filtrate was then neutralised with sodium hydrogen carbonate and extracted with ether. *Hexa-acetyl-lactal* ("acetolactal"),  $C_{22}H_{32}O_{15}$ , has m. p. 113—114° (corr.), and the optically pure specimens obtained after six recrystallisations from alcohol have  $[\alpha]_D^{20} - 12.27^\circ$ ,  $-12.14^\circ$ , in *s*-tetrachloroethane. It absorbs bromine, forming a *dibromide*, which separates in microscopic, thin prisms, m. p. 207° (corr., decomp.),  $[\alpha]_D^{20} + 135.5^\circ$ ,  $[\alpha]_D^{25} + 135.7^\circ$ , in *s*-tetrachloroethane. When left with barium hydroxide solution at 37°, it is hydrolysed to *lactal*,  $C_{12}H_{20}O_9$ , which crystallises with  $1H_2O$ , in slender, white prisms, m. p. 184—186° (corr.), whilst the anhydrous compound, obtained in a high vacuum, is pale yellow and has m. p. 165—170° (decomp.). For the hydrate, the values  $[\alpha]_D^{20} + 26.92^\circ$  and  $+26.77^\circ$  were obtained, and for the anhydride,  $[\alpha]_D^{20} + 28.53^\circ$ , or, calculated for the hydrate,  $+26.95^\circ$ . The agreement in rotation is strange, seeing that the compounds differ so widely in m. p.'s. Lactal is faintly sweet, does not give the pine-splinter test, and is practically indifferent towards Fehling's solution or phenylhydrazine, but it resembles glucal in that its solutions restore the colour to Schiff's reagent, decolorise bromine water, and become dark on warming with hydrochloric acid.

Hexa-acetyl-lactal is quickly reduced in presence of spongy platinum to *hexa-acetylhydrolactal*,  $C_{24}H_{34}O_{15}$ , a colourless powder which softens at 50—60°, and is readily hydrolysed by baryta water at 37°. *Hydrolactal*,  $C_{12}H_{22}O_9$ , is also most readily obtained by the reduction of lactal. It crystallises from 80% alcohol in slender prisms, with  $1H_2O$ ,  $[\alpha]_D^{20} + 26.82^\circ$ ,  $[\alpha]_D^{25} + 26.79^\circ$ , 26.58°, in water, and this hydrate, like the anhydride, has m. p. 204—205° (corr.). It has none

of the aldehydic and reducing properties of lactal, but is hydrolysed by dilute acids, the production of galactose being proved by the isolation of mucic acid on evaporation with dilute nitric acid. It was found to be extremely difficult actually to separate the products of hydrolysis, but, after destroying the galactose produced by the action of emulsin, by yeast fermentation, a good yield of hydroglucal could be isolated from the residue.

J. C. W.

**Cellobial and Hydrocellobial.** EMIL FISCHER and KÁLMÁN VON FODOR (*Ber.*, 1914, 47, 2057—2063).—Acetobromocellobiose has been reduced and submitted to the further treatment which was described in the cases of dextrose (A., 1913, i, 445; this vol., i, 252) and lactose (preceding abstract). The relation of hydrocellobial to hydrolactal and hydroglucal is demonstrated by the formation of a reducing sugar and of hydroglucal by the action of emulsin.

Analytically pure acetobromocellobiose should be used in the reduction, since the presence of unchanged octa-acetylcellobiose hinders the purification of the new products.

*Hexa-acetylcellobial*,  $C_{12}H_{14}O_9Ac_6$ , separates from chloroform and petroleum in small, rhombic leaflets, m. p. 134—135° (corr.),  $[\alpha]_D^{17} - 19.8^\circ$ ,  $-19.6^\circ$ , in *s*-tetrachloroethane, and forms a *dibromide*, in very pale yellow, microscopic prisms, m. p. 165—166° (corr.),  $[\alpha]_D^{20} + 57.9^\circ$ ,  $+57.4^\circ$ . When left with baryta water, it is hydrolysed to *cellobial*,  $C_{12}H_{20}O_9$ , which forms colourless prisms, m. p. 175—176° (corr.),  $[\alpha]_D^{25} + 1.0^\circ$ , in water, and reacts like lactal.

*Hexa-acetylhydrocellobial*,  $C_{12}H_{16}O_9Ac_6$ , is obtained, by catalytic reduction, in colourless, microscopic prisms or tablets, m. p. 133—134°,  $[\alpha]_D^{19} + 11.2^\circ$ ,  $[\alpha]_D^{18} + 11.1^\circ$ , in *s*-tetrachloroethane, and *hydrocellobial*,  $C_{12}H_{22}O_9$ , crystallises in colourless prisms, m. p. 222° (corr.),  $[\alpha]_D^{18} + 4.3^\circ$ ,  $[\alpha]_D^{21} + 4.1^\circ$ , in water. After hydrolysis by emulsin, followed by destruction of the dextrose by yeast, hydroglucal was isolated in good yield.

J. C. W.

**Action of Concentrated Sulphuric Acid on Cellulose.** S. TSCHUMANOV (*Kolloid. Zeitsch.*, 1914, 14, 321—322).—In reference to the preparation of colloidal carbon by the action of sulphuric acid on sucrose (Sabbatani, this vol., ii, 198), the author communicates observations relative to the action of the concentrated acid on cellulose. Strips of filter paper were left for some days in contact with the acid, and the resulting dark-coloured liquid then treated with a large volume of water. The precipitate, washed until free from sulphuric acid, and dried at 100—112° until the weight became constant, was found to contain C 62.1%, H 5.0%, and O 32.9%, corresponding with the formula  $(C_2H_2O)_n$ .

At the end of two and a-half years it was found that the liquid obtained from 2.59 grams of cellulose and 100 c.c. of acid had solidified to a gelatinous mass.

H. M. D.

**Action of Ammoniacal Copper Hydroxide on Cellulose.** EDM. CONNERADE (*Bull. Soc. chim. Belg.*, 1914, 28, 176—186).—Experiments have been made on the solubility of cellulose in ammoniacal copper hydroxide, and on the relationships existing between the concentrations

of ammonia, copper and the quantity of cellulose dissolved. It is shown that a solution of ammoniacal cuprous hydroxide, prepared at low temperatures, contains, in comparison with cupric hydroxide, a large excess of colloidal ammoniacal cuprous hydroxide. The cupric hydroxide only plays a secondary part in the solution of the cellulose. The solubility of cellulose is proportional to the concentration of the colloidal ammoniacal cuprous hydroxide. The solution of cellulose is brought about by the combination of quantities of colloidal ammoniacal cuprous hydroxide and water in amounts which increase to a point at which an equilibrium exists between the liquid and solid phases. The strongly hydrated colloidal complex combines with ammonia in proportion to its concentration, and this tends to render the complex more stable. The coagulation of the colloidal complex can be effected reversibly in solution.

J. F. S.

The Asymmetric Cobalt Atom. K. A. WERNER [with H. KUH and P. WÜST] (*Ber.*, 1914, 47, 1961—1979).—The tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte salts have the constitutional formula  $\left[ \text{en}_2 \overset{\text{III}}{\text{Co}} \begin{array}{c} \text{NH}_2 \\ \text{O}_2 \end{array} \overset{\text{IV}}{\text{Co}} \text{en}_2 \right] \text{X}_4$  (compare A., 1910, ii,

857). Calling the two radicles  $\left( \text{en}_2 \overset{\text{III}}{\text{Co}} \right)$  and  $\left( \text{en}_2 \overset{\text{IV}}{\text{Co}} \right)$ , A and B, four optically active series of isomerides should exist, namely: + A + B, - A - B, + A - B, and - A + B. Hitherto only the first two series and the corresponding racemates have been isolated. The resolution was accomplished by treating the aqueous solution of the bromide with *d*- or *l*-bromocamphorsulphonate. The filtrate from the precipitate was fractionally crystallised, and the precipitate, which contained the tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte bromosulphonates besides silver bromide, was fractionally extracted with hot water and the extracts fractionally crystallised. The final yield was very small, but the pure *d*- and *l*-bromocamphorsulphonates of the isomeric dicobalt salts were obtained, either in dark green leaflets or in olive-green needles, the former being the more readily soluble. The specific rotatory powers were:

	From <i>d</i> -acid.	From <i>l</i> -acid.
Leaflets . . . .	+ 520°	- 520°
Needles . . . .	- 280°	+ 280°

The bromides prepared from these had  $[\alpha] \pm 840^\circ$ ,  $[M] \pm 6855^\circ$ , which is the greatest rotatory power hitherto observed. This high activity is connected with the presence of quadrivalent cobalt in the molecule, since when it is reduced to the trivalent condition the activity diminishes considerably.

The active tetraethylenediamine- $\mu$ -aminoperoxocobalticobalte salts are fairly stable in aqueous solution, but after keeping the solution for some weeks the activity completely disappears. This loss of activity is accompanied by decomposition, the olive-green solutions changing to a brownish-yellow colour.

By the action of ammonia the active tetraethylenediamine- $\mu$ -imino-

peroxocobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{O}_2 \end{array} \text{Co en}_2 \right] \text{X}_3$ , are obtained from the aminoperoxocobaltic salts. A change of rotation occurs, the *d*- and *l*-aminoperoxo-salts giving respectively the *l*- and *d*-iminoperoxosalts. At the same time the rotation diminishes considerably, the iodides having  $[\alpha] \pm 166^\circ$ ,  $[\text{M}] \pm 1372^\circ$ . Also the active aminoperoxo-salts could be converted into the valency isomeric, red tetraethylenediamine- $\mu$ -ammoniumperoxo-salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{O}_2 \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{Co en}_2 \right] \text{X}_3$ ;

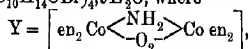
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again, there is a change in the sign of, and a diminution in, the rotation, the dithionates having  $[\alpha] \pm 192^\circ$ ,  $[\text{M}] \pm 1625^\circ$ . Comparing the bromides of the green aminoperoxo- and the red ammoniumperoxo-series, the change in molecular rotation is from  $-6654^\circ$  to  $+1510^\circ$ , a total change of  $8364^\circ$ , thus showing the astonishingly great effect which a change from principal to subsidiary valency has on the optical rotation.

From the active  $\mu$ -aminoperoxo-salts were also prepared the active  $\mu$ -amino-ol-dicobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array} \text{Co en}_2 \right] \text{X}_4$ , the active  $\mu$ -aminonitrodicobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{array} \text{Co en}_2 \right] \text{X}_4$ , and the active  $\mu$ -amino-sulphatodicobaltic salts,  $\left[ \text{en}_2 \text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{SO}_4 \end{array} \text{Co en}_2 \right] \text{X}_5$ . In each case there is a change in the sign of, and a considerable diminution in, the rotation.

The relation between the rotatory powers in the various series has still to be studied with homogeneous light, since the rotation dispersion is great in all cases. For example, in the  $\mu$ -aminoperoxo-series the values  $[\alpha]_D^{19} + 814.4^\circ$  and  $[\alpha]_E^{19} + 1200^\circ$ , were observed.

*d*-Tetraethylenediamine- $\mu$ -aminoperoxocobaltic-*d*-bromocamphorsulphonate,  $\text{Y} (\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr})_4 \cdot 9\text{H}_2\text{O}$ , where



forms dark green leaflets;  $[\alpha]^{20} + 520^\circ$ ,  $[\text{M}]^{20} + 9734.4^\circ$ . The corresponding *ld*-salt,  $\text{Y} (\text{SO}_3 \cdot \text{C}_{10}\text{H}_{14}\text{OBr})_4 \cdot 8\text{H}_2\text{O}$ , crystallises in olive-green needles, and has  $[\alpha]^{20} - 280^\circ$ ,  $[\text{M}]^{20} - 5191.2^\circ$ . The *d*- and *l*-bromides,  $\text{YBr}_4 \cdot 5\text{H}_2\text{O}$ , prepared from the bromocamphorsulphonates by double decomposition with sodium bromide, form greenish-black, glistening prisms,  $[\alpha]^{17} \pm 840^\circ$ ,  $[\text{M}]^{17} \pm 6854.4^\circ$ . The *d*- and *l*-dithionates,  $\text{Y} (\text{S}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ , gives greenish-black, glistening crystals, and have respectively  $[\alpha]^{17} + 848^\circ$ ,  $[\text{M}]^{17} + 6919.6^\circ$ , and  $[\alpha]^{22} - 840^\circ$ ,  $[\text{M}]^{22} - 6854.4^\circ$ . The *d*- and *l*-nitrates,  $\text{Y} (\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ , consist of crystalline, light olive-green powders, and have  $[\alpha]^{17} \pm 920^\circ$ ,  $[\text{M}]^{17} \pm 6348^\circ$ .

Further investigation of the racemic tetraethylenediamine- $\mu$ -aminoperoxocobalticcobalt bromide (compare *loc. cit.*) shows that it possesses six molecules of water of crystallisation and not five as previously stated. The *r*-chloride,  $\text{YCl}_4 \cdot 6\text{H}_2\text{O}$ , obtained from the bromide and silver chloride, forms dark green, regular, cube-shaped crystals. The *r*-dithionate,  $\text{Y} (\text{S}_2\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$ , gives dark-green crystals, and the *r*-platini-

chloride,  $Y(PtCl_6)_2 \cdot 3H_2O$ , glistening, slender leaflets, with a greenish shimmer.

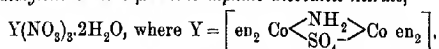
d- and l-Tetraethylenediamine- $\mu$ -iminoperoxo-cobalticobaltic iodides,  $\left[ en_2 Co \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ O_2 \end{array} Co en_2 \right] I_3 \cdot 4H_2O$ , are obtained by dissolving respectively the l- and d- $\mu$ -aminoperoxo-bromides in concentrated ammonia and precipitating the filtered solution with ammonium iodide. They form dark brown needles,  $[\alpha]^{17} \pm 160^\circ$ ,  $[M]^{17} \pm 1372.8^\circ$ .

d- and l-Tetraethylenediamine- $\mu$ -ammoniumperoxocobalticobaltic bromides,  $\left[ en_2 Co \begin{array}{c} O_2 \\ \diagup \quad \diagdown \\ \text{NH} \\ | \\ HBr \end{array} Co en_2 \right] Br_3 \cdot 5H_2O$ , were obtained in an impure

condition by dissolving the respective l- and d- $\mu$ -aminoperoxo-bromides in concentrated ammonia, and then treating the cooled solution with concentrated hydrobromic acid until the reddish-brown colour of the solution changed to red. On trituration, the reddish-brown, impure bromide crystallised out. The pure d-bromide was obtained by transforming the impure salt into the dithionate and then converting the latter back into the bromide. It is a bright red, crystalline powder,  $[\alpha]^{19} + 208^\circ$ ,  $[M]^{19} + 1510^\circ$ . The pure l-bromide was not obtained, owing to insufficient material. The d- and l-dithionates,

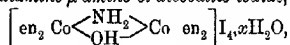
$en_2 Co \begin{array}{c} O_2 \\ \diagup \quad \diagdown \\ \text{NH} \\ | \\ H \end{array} Co en_2 \left[ \begin{array}{c} S_2O_6 \\ | \\ S_2O_6 \end{array} \right] \cdot 7H_2O$ , crystallise in salmon-coloured, slender needles,  $[\alpha]^{13} \pm 192^\circ$ ,  $[M]^{13} \pm 1625.8^\circ$ .

r-Tetraethylenediamine- $\mu$ -aminosulphato-dicobaltic nitrate,



is obtained from the  $\mu$ -aminoperoxo-nitrate by dissolving the latter in a concentrated solution of sulphur dioxide. Solution takes place with development of heat, and, on cooling, reddish-brown crystals separate. Further treatment with sulphur dioxide gives a red salt, from the aqueous solution of which, concentrated nitric acid precipitates the required nitrate as light-red needles. The bromide was obtained from the nitrate by double decomposition with ammonium bromide, and from the bromide, the d-bromocamphorsulphonate,  $Y(SO_3 \cdot C_{10}H_{14}OBr)_3 \cdot 4H_2O$ , was prepared; it forms light-red needles, and is not resolved into the active isomerides by fractional recrystallisation. The active d-nitrate,  $Y(NO_3)_3 \cdot 2H_2O$ , was, however, obtained from l-tetraethylenediamine- $\mu$ -aminoperoxo-cobalticobaltic nitrate by treatment with sulphur dioxide, as for the racemic nitrate. It crystallises in well developed, red prisms;  $[\alpha] + 200^\circ$ ,  $[M] + 1384^\circ$ .

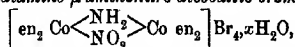
d-Tetraethylenediamine- $\mu$ -amino-ol-dicobaltic iodide,



is obtained as follows: the l- $\mu$ -aminoperoxo-nitrate is dissolved in water containing acetic acid and the black periodide obtained by treatment with sodium iodide. Sodium thiosulphate is then added until the solution and salt become red, after which the solution is saturated with

sodium iodide. On recrystallisation from water, the iodide forms bluish-red leaflets, and has  $[\alpha]^{20} + 110^\circ$ ,  $[M]^{20} + 990^\circ$ . The salts are being further investigated.

*d-Tetraethylenediamine- $\mu$ -aminonitro-dicobaltic bromide,*



is obtained from an aqueous solution of the *l*- $\mu$ -aminoperoxo-bromide by treatment with sodium nitrite, followed by concentrated hydrobromic acid. It forms dark-red cubes, and has  $[\alpha]^{19} + 158^\circ$ ,  $[M]^{19} 1311.4^\circ$ .

In the resolution of the salts of the tetraethylenediamine  $\mu$ -aminoperoxo-series, brownish-green and brown needles were obtained as an impurity. They were purified by a complicated process and shown not to be isomeric with the green salts, but their constitution has not yet been elucidated.

T. S. P.

The Asymmetric Cobalt Atom. XI. Oxalatodiethylenediaminecobaltic Salts, and a New Method for Resolving Racemic Inorganic Compounds. A. WERNER [with J. BOSSEHART] (*Ber.*, 1914, 47, 2171—2182).—The study of the active oxalatodiethylenediaminecobaltic salts (Werner and McCutcheon, A., 1913, i, 19) has again been undertaken in order to investigate the separation of the active compounds from the racemates by crystallisation methods. The bromide was found to give the best results, 100 grams of water at  $17^\circ$  dissolving 1.05 grams of the *d*-bromide and 1.85 grams of the *r*-bromide respectively. The pure active bromide was readily obtained from the impure salt by fractional crystallisation and served for the preparation of other salts (see later).

The great difference in solubility of the active and racemic bromides led the authors to investigate the preparation of the active bromide by precipitation of the aqueous solution with alcohol, or with a mixture of alcohol and ether. If the solution contains the racemate and an excess of the *d*-salt, the latter is readily precipitated, but the mother liquor, instead of being inactive, is found to be levorotatory, and further precipitation with alcohol and ether gives the *l*-salt, which is obtained pure by one more precipitation. The same thing holds good if a mixture of the *l*-salt and the racemate is fractionally precipitated, the *l*-salt being first obtained and then the *d*-salt. Thus by simple precipitation of a mixture of an active salt and the racemate, resolution of the racemate takes place. Similar results are obtained with dinitrodiethylenediaminecobaltic chloride, and as a general result it may be stated that resolution takes place in this manner when the active salt is less soluble than the racemate. If the racemate is the more soluble salt, no resolution takes place.

It is not necessary for the active salt to belong to the same series of salts as the racemate for resolution of the latter to take place. For example, if a mixture of *d*-oxalatodiethylenediaminecobaltic chloride with *r*-dinitrodiethylenediaminecobaltic chloride is fractionally precipitated with alcohol, the first precipitate consists of a mixture of *d*-oxalato-chloride and *d*-dinitro-chloride, which are readily separated, owing to their differing solubilities; from the mother liquor the *l*-dinitro-chloride is obtained.

In a similar manner the active salt of one metal can be used to resolve the racemate of another metal. In this way *r*-oxalatodiethylenediaminechromium bromide has been resolved by the addition of one-*seventh* of its weight of *d*-oxalatodiethylenediaminecobaltic bromide. The *l*-cobalt salt is less soluble than the *d*-chromium salt, which latter is therefore readily obtained pure. By the addition of active chromium salts thus obtained to further quantities of the racemate, the latter can readily be resolved.

The above methods of resolving racemates must be further studied before a theoretical interpretation of the results can be given; in some respects they are similar to the results obtained with other compounds by Ostromisslenski (A., 1908, ii, 913).

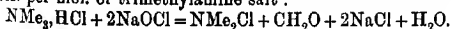
Werner and McCutcheon (*loc. cit.*) investigated the rotatory power of the active oxalatodiethylenediaminecobaltic salts towards white light. Using monochromatic light the dispersion is found to be very marked, as the following results show.

*d*-Oxalatodiethylenediaminecobaltic chloride,  $[C_2O_4 Co en_2]Cl$ , has  $[a]_D + 848^\circ$ ,  $[M]_D + 2561^\circ$ ,  $[a]_C + 308^\circ$ ,  $[M]_C + 930^\circ$ ; the corresponding *l*-chloride has  $[a]_D - 840^\circ$ ,  $[M]_D - 2536^\circ$ ,  $[a]_C - 304^\circ$ ,  $[M]_C - 918^\circ$ . Equimolecular quantities of the active salts, when mixed, give prisms of the inactive racemate. The *d*-bromide,  $[C_2O_4 Co en_2]Br$ , which was obtained from the chloride by treatment with concentrated hydrobromic acid, has  $[a]_D + 736^\circ$ ,  $[M]_D + 2546^\circ$ ,  $[a]_C + 268^\circ$ ,  $[M]_C + 927^\circ$ ; the corresponding *l*-bromide has  $[a]_D - 728^\circ$ ,  $[M]_D - 2518^\circ$ ,  $[a]_C - 269^\circ$ ,  $[M]_C - 899^\circ$ . From the *d*- and *l*-bromides the following salts were prepared by double decomposition with the alkali metal salts of the appropriate acids. *d*-Oxalatodiethylenediaminecobaltic perchlorate,  $YClO_4 \cdot H_2O$ , where  $Y = [C_2O_4 Co en_2]$ , forms long needles, and has  $[a]_D + 688^\circ$ ,  $[M]_D + 2518^\circ$ ,  $[a]_C + 240^\circ$ ,  $[M]_C + 878^\circ$ ; the *l*-perchlorate has  $[a]_D - 686^\circ$ ,  $[M]_D - 2547^\circ$ ,  $[a]_C - 248^\circ$ ,  $[M]_C - 907^\circ$ . The *d*- and *l*-thiocyanates,  $YSCN$ , crystallise in leaflets and have  $[a]_D \pm 784^\circ$ ,  $[M]_D \pm 2548^\circ$ ,  $[a]_C \pm 280^\circ$  and  $-284^\circ$ ,  $[M]_C \pm 910^\circ$  and  $-923^\circ$ . The *d*- and *l*-dithionates,  $Y_2S_2O_6$ , form short, glistening needles, and have  $[a]_D + 600^\circ$  and  $596^\circ$ ,  $[M]_D + 2562^\circ$  and  $-2544^\circ$ ,  $[a]_C + 216^\circ$  and  $-212^\circ$ ,  $[M]_C + 922^\circ$  and  $-905^\circ$ . The *d*- and *l*-iodides,  $YI$ , form a dull, crystalline powder, and have  $[a]_D + 640^\circ$  and  $-644^\circ$ ,  $[M]_D + 2521^\circ$  and  $-2537^\circ$ ,  $[a]_C \pm 232^\circ$ ,  $[M]_C \pm 914^\circ$ . The *d*- and *l*-nitrates,  $YNO_3 \cdot xH_2O$ , crystallise in long, dark-red needles, and have  $[a]_D \pm 724^\circ$ ,  $[M]_D \pm 2512^\circ$ ,  $[a]_C \pm 264^\circ$ ,  $[M]_C \pm 916^\circ$ .

*d*- and *l*-Oxalatodiethylenediaminechromic bromides,  $[C_2O_4 Cr en_2]Br$ , form orange-red powders, and have  $[a]_D + 332^\circ$  and  $-316^\circ$ ,  $[M]_D + 1129^\circ$  and  $-1075^\circ$ ,  $[a]_C + 164^\circ$  and  $-156^\circ$ ,  $[M]_C + 557^\circ$  and  $-530^\circ$ . Their aqueous solution rapidly undergoes racemisation.

T. S. P.

Preparation of Dimethylamine and Dimethylaminomethyl Alcohol. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 269430. Compare this vol., i, 150).—The yield of dimethylaminomethyl alcohol may be raised from about 30% to almost its theoretical value by increasing the amount of hypochlorite or hypobromite used to 2 mols. per mol. of trimethylamine salt:





The halogenated dimethylamine may be separated and reduced by means of a sulphite or hydrogen sulphite or zinc dust to dimethylamine, or the liquid may be treated directly with the reducing agent and then rendered alkaline, in order to obtain dimethylaminomethyl alcohol.

T. H. P.

**Preparation of Betaine Salts.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 269338).—When treated with a methyl haloid in presence or absence of an indifferent organic solvent, methyl dimethylaminoacetate is readily converted into the methyl ester of the corresponding halogen salt of betaine. This ester is hydrolysed by heating its aqueous solution, preferably acidified with a mineral acid, the betaine salt being thus obtained in almost quantitative yield.

T. H. P.

**The Esters of Choline.** E. FOURNEAU and HAROLD J. PAGE (*Bull. Soc. chim.*, 1914, [iv], 15, 544–553).—The authors have prepared a number of esters of choline with the view of studying their hæmolytic properties as compared with those of lysocithin (compare this vol., i, 781). A number of these esters have been previously studied from the point of view of their effect on blood pressure, but have apparently never been isolated except in the form of their platinichlorides or aurichlorides, and these not characterised. The chlorides, bromides, and iodides of a number of choline esters have been prepared by the action of trimethylamine on the chloro- or iodo-ethyl esters of the higher fatty acids, the latter having been first prepared by the condensation of  $\beta$ -chloro- or iodo-ethyl alcohol with the acid chlorides. The following halogen-ethyl esters were prepared:  $\beta$ -chloroethyl stearate,  $C_{17}H_{35}CO_2 \cdot C_2H_4Cl$ , voluminous plates, m. p.  $49.5^\circ$ ;  $\beta$ -chloroethyl palmitate, nacreous plates, m. p.  $41.5^\circ$  (compare Krafft, A., 1904, i, 136);  $\beta$ -chloroethyl dodecoate, a liquid, b. p.  $165^\circ/19$  mm., m. p.  $17^\circ$  (Krafft, *loc. cit.*);  $\beta$ -chloroethyl octoate, a liquid, b. p.  $135^\circ/18$  mm.;  $\beta$ -iodoethyl stearate, nacreous plates, m. p.  $59.5^\circ$ ;  $\beta$ -iodoethyl palmitate, m. p.  $54^\circ$ ;  $\beta$ -iodoethyl tetradecoate, m. p.  $45.5^\circ$ ;  $\beta$ -iodoethyl dodecoate, m. p.  $35^\circ$ ;  $\beta$ -iodoethyl nonoate, b. p.  $169^\circ/15$  mm.;  $\beta$ -iodoethyl octoate, b. p.  $170^\circ/26$  mm.;  $\beta$ -iodoethyl butyrate, b. p.  $100^\circ/16$  mm.;  $\beta$ -iodoethyl oleate, a very viscous liquid, crystallising at  $6^\circ$ , but which could not be purified.

All the iodoethyl esters readily react with trimethylamine on heating in benzene solution in sealed tubes at  $100^\circ$ , giving the corresponding alkyloxycholine iodides; but of the chloroethyl esters, only those which are esters of the  $C_8$  or lower acids give this reaction. The choline chlorides can, however, be prepared from the corresponding iodides by shaking their solutions in methyl alcohol with excess of silver chloride. All the iodides prepared were hygroscopic, but not deliquescent, whilst the chlorides below the term in  $C_{12}$  were deliquescent and difficult to purify. All the salts were soluble in water, giving solutions, soapy to the touch and frothing on shaking. The chlorides of the higher members melt to very viscous, transparent, highly-refractive liquids at a relatively low temperature, fairly well-defined, and on heating to about  $200^\circ$  the liquids become mobile,

much gas is evolved, and the residues solidify. Concentrated aqueous solutions of the chlorides or iodides do not give a precipitate with silver nitrate, the silver haloid being kept in colloidal solution until alcohol is added.

The following substituted choline salts and their derivatives have been prepared:

*Stearylcholine iodide*, nacreous plates, yielding with silver chloride the *chloride*, long prisms, first m. p.,  $73^{\circ}$ , second m. p.,  $193^{\circ}$ , which gives an *aurichloride*, rhombohedra, m. p.  $109-110^{\circ}$ , a *platinichloride*, hexagonal plates, m. p.  $218^{\circ}$ , and a *picrate*, m. p.  $102^{\circ}$ .

*Palmitylcholine iodide*, nacreous plates, giving the *chloride*, prismatic needles, first m. p.,  $66^{\circ}$ , second m. p.,  $194.5^{\circ}$ , giving an *aurichloride*, large plates, m. p.  $110^{\circ}$ , a *platinichloride*, slender needles, m. p.  $218^{\circ}$ , and a *picrate*, m. p.  $101.5^{\circ}$ .

*Dodecylcholine iodide* and the *chloride*, long plates, first m. p.,  $54^{\circ}$ , second m. p.,  $196^{\circ}$ , giving an *aurichloride*, rectangular plates, m. p.,  $106^{\circ}$ , a *platinichloride*, slender needles, m. p.  $117^{\circ}$ , and a *picrate*, rhombic plates, m. p.  $97.5^{\circ}$ .

*Octylcholine iodide* and the *chloride*, first m. p.,  $35^{\circ}$ , second m. p.,  $198^{\circ}$ , giving an *aurichloride*, lenticular, rhombic plates, m. p.  $87-88^{\circ}$ , a *platinichloride*, long, prismatic needles, m. p.  $203-204^{\circ}$ , and a *picrate*, rhombic plates, m. p.  $94^{\circ}$ .

*Butylcholine iodide* and the *chloride*, large, very deliquescent, prismatic needles, giving an *aurichloride*, rhombic plates, m. p.  $93-94^{\circ}$ , a *platinichloride*, long, rectangular prisms, m. p.  $209^{\circ}$ , and a *picrate*, rectangular plates.

*Oleylcholine iodide*, crystallising in stout plates, and the *chloride*, which yields a *platinichloride*, short prisms, m. p.  $104-105^{\circ}$ , and a *picrate*, rectangular plates, m. p.  $88-89^{\circ}$ .

*Acetylcholine bromide*, crystallising in deliquescent, rectangular prisms.

*Tetradecylcholine chloride*, plates, first m. p.,  $58^{\circ}$ , second m. p.,  $195^{\circ}$ , giving an *aurichloride*, thin plates, m. p.  $108-109^{\circ}$ , a *platinichloride*, long needles, m. p.  $217.5^{\circ}$ , and a *picrate*, rhombic plates, m. p.  $98.5^{\circ}$ .

*Acetylcholine chloride* was prepared by the interaction of trimethylamine and chloroethylacetate, but could not be purified on account of the readiness with which it hydrolysed.

*Benzoylcholine chloride*, long, transparent prisms, m. p.  $200^{\circ}$  (decomp.), gives an *aurichloride*, silky needles, m. p.  $182^{\circ}$ , a *platinichloride*, small rhombohedra, m. p.  $224^{\circ}$ , and a *picrate*, rectangular plates.

The hæmolytic properties of these choline derivatives is being studied, and at present it can only be stated that the hæmolyzing powers of the palmityl and stearyl derivatives are but little inferior to those of lysocithin (compare *loc. cit.*). W. G.

**Preparation of  $\alpha$ -Dichloroisopropyl Carbamate.** BRUNO BECKMANN, CHEMISCHE FABRIK (D.R.-P. 271737).—The compound,  $\text{NH}_2\text{COO}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ , m. p.  $82-83^{\circ}$ , obtained from chloroformamide and  $\alpha$ -dichloropropan- $\beta$ -ol, differs from Otto's dichloroisopropyl carbamate (A., 1891, 1373), in its melting point, its solubility, and its bitter taste. T. H. P.

**Creatine and Creatinine Metabolism. I. The Preparation of Creatine and Creatinine from Urine.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1914, 18, 183—190).—New methods for the preparation of creatine and creatinine from urine are described in detail. The zinc chloride compound is first formed, and from this, creatine is obtained by boiling with calcium hydroxide, and creatinine, in 60—80% yield, by dissolving in concentrated ammonia and allowing to cool in ice. The creatinine which crystallises out is usually quite pure, but may be recrystallised from warm concentrated ammonia.

H. W. B.

**Effect of Formaldehyde on Sheep's Wool and Constitution of the Latter.** ALBERT KANN (*Chem. Zentr.*, 1914, i, 1193; from *Färber-Zeit.*, 25, 73—75).—Small quantities of formaldehyde (up to 0.1% commercial formaldehyde by weight) render sheep's wool less sensitive to alkali, etc., without influencing its behaviour towards dyes, and this property is not affected by a preliminary treatment of the wool with nitrous acid. Wool treated with formaldehyde gives the same yellow colour with nitrous acid as the untreated product. The author is led to the conclusion that nitrous acid behaves as a nitrosating and not as a diazotising agent, and that formaldehyde causes an aldol condensation. The wool molecule therefore contains imino- and carboxy-, not amino- and keto-groups. Acetaldehyde behaves similarly but more weakly, whilst acraldehyde has a more powerful action than formaldehyde. The greatest resistance to alkali is developed in wool which has been previously treated with weak formaldehyde and is subsequently subjected to the action of the aldehyde in the alkaline bath.

H. W.

**Synthesis of Polypeptides by the Action of Glycerol on Glycine.** L. C. MAILLARD (*Ann. Chim.*, 1914, [ix], 1, 519—578).—A fuller account of work already published (compare A., 1912, i, 13).

W. G.

**Preparation and New Reactions of the Esters of Hydrazinocarboxylic Acids.** OTTO DIELS (*Ber.*, 1914, 47, 2183—2195).—Although at higher temperatures the alkyl carbonates and hydrazine give rise exclusively to carbonylhydrazide, at the ordinary temperature or at 0°, excellent yields of alkyl hydrazinocarboxylates are obtainable. These compounds, of which the ethyl member has already been described (Diels, A., 1903, i, 324; Gutmann, *Dis.*, Heidelberg, 1903), are colourless, crystalline solids.

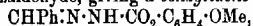
When ethyl carbonate is shaken with hydrazine hydrate and the mixture kept at the ordinary temperature for about seven hours, the resultant clear liquid on distillation yields ethyl hydrazinocarboxylate,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p. 45°, b. p. 93°/9 mm., 108—109°/22 mm., in almost theoretical quantity. On distillation under ordinary pressure, the ester undergoes partial decomposition with formation of ethyl

hydrazinodicarboxylate, m. p. 132°, and urazine,  $\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{>NH}\cdot\text{NH}_2$ , (Busch, A., 1907, i, 564), m. p. 270°.

Methyl carbonate and hydrazine hydrate when shaken together give a homogeneous mixture in a very short time, subsequent distillation under reduced pressure leaving a residue of *methyl hydrazinocarboxylate*,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , m. p. 73°, in 90—95% yield. At 150° the hydrochlorides of the ethyl and methyl esters undergo decomposition, in which the corresponding alkylhydrazine is formed, the yield of pure methylhydrazine from 52 grams of the hydrochloride of the methyl ester being 3—4 grams.

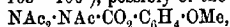
*o*-Methoxyphenyl hydrazinocarboxylate,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , obtained by the interaction of hydrazine hydrate and guaiacyl carbonate in the presence of alcohol at 0°, forms lustrous prisms, m. p. 99—100°; it decomposes near 160°, giving a distillate of guaiacol, the residue being a brittle, amorphous substance of the composition  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})(\text{CH}_3\text{ON})_{10}$ , the brown solution of which in solutions of an alkali on the addition of a little Fehling's solution changes to a deep olive-brown, the colour passing into a violet where the wall of the test glass is wet with a film of the liquid. The amorphous substance appears to dissolve unchanged in cold water, but, on warming, decomposition ensues with formation of guaiacol and a sparingly soluble substance of the composition  $(\text{CH}_3\text{ON})_2$ ; this is a heavy, crystalline powder, and gives the same effect as the amorphous compound with alkali and Fehling's solution.

In hot alcoholic solution *o*-methoxyphenyl hydrazinocarboxylate condenses with benzaldehyde, giving a *benzylidene* derivative,

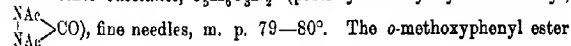


a colourless, crystalline solid, m. p. 176°, to a yellow fluid, with previous sintering at 168°. When heated under a pressure of 14 mm. at 185°, decomposition ensues, giving an almost quantitative yield of guaiacol and a very sparingly soluble substance,  $\text{C}_8\text{H}_6\text{ON}_2$ , prisms or needles, m. p. 268—269° (decomp.), whilst a small amount of benzaldazine is also produced.

If *o*-methoxyphenyl hydrazinocarboxylate is heated with acetic anhydride and the resulting liquid is distilled under reduced pressure, the *acetyl* compound present undergoes decomposition between 125° and 220° giving guaiacol, guaiacyl acetate, a substance,  $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2$  (well formed crystals, m. p. 105—106°), possibly of the structure



and another substance,  $\text{C}_8\text{H}_6\text{O}_3\text{N}_2$  (possibly diacetyl-hydrazicarbonyl,



similarly gives a *formyl* derivative,  $\text{CHO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , quadrate tablets, m. p. 114—115° with previous sintering at 110°, which when heated at 160—220°/14 mm. decomposes with the formation of guaiacol and a substance,  $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$  (possibly formylhydrazicarbonyl,  $\begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{>N}\cdot\text{CHO}$ ), stout, colourless, prismatic crystals, m. p. 120°; some-

what resembling alum in taste.

D. F. T.

Transformation of *d*-isopropylmalonic Acid into its Optical Antipodes by Interchanging the Carboxyl and Amido-groups. EMIL FISCHER and FRITZ BRAUNS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 714—727).—An attempt was recently made to interchange the amido- and carboxyl groups in an active amic acid, in order to determine whether inversion would thereby result, in accordance with the theory of the asymmetric carbon atom (this vol., i, 247). This has now been accomplished in the case of *d*-isopropylmalonic acid by the following series of reactions. The acid was converted into the methyl ester, the amido-group was replaced by carboxyl, and then, instead of treating the ester with ammonia, wherein lay the failure at the previous attempt, it was mixed with hydrazine and the hydrazide was converted into the azoimide. This reacted readily with ammonia, with the formation of the optical isomeride of the original acid. The reactions were first investigated in the racemic series, and then carried through with the *d*-acid in much the same way.

Ethyl  $\alpha$ -cyanoisovalerate (A., 1909, i, 628) was heated with concentrated sulphuric acid on the water-bath for twenty hours, and then poured on ice, when isopropylmalonic acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{CHPr}^d\cdot\text{CO}_2\text{H}$ , crystallised from the solution. The acid separated from water in envelope-shaped crystals, m. p.  $158^\circ$  (corr., decomp.), and, by treatment with diazomethane in methyl acetate suspension, yielded the methyl ester, slender needles, m. p.  $121^\circ$  (corr.). This was suspended in cold ether and treated with nitrous fumes until a clear solution resulted, whereby it was transformed into methyl hydrogen isopropylmalonate,  $\text{CO}_2\text{Me}\cdot\text{CHPr}^d\cdot\text{CO}_2\text{H}$ , b. p.  $95\text{--}100^\circ$  (bath)/0.3 mm.,  $D_4^{1.055}$ . This was mixed with anhydrous hydrazine at  $0^\circ$ , and left for a day, when the excess of the base was removed in a vacuum. The solid hydrazide which remained was dissolved in water and precipitated with lead acetate, when the lead salt separated in sparkling leaflets. The free isopropylmalonhydrazidic acid,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CHPr}^d\cdot\text{CO}_2\text{H}$ , which formed glistening leaflets, m. p.  $172^\circ$  (corr.), was suspended in water, shaken with sodium nitrite until dissolved, and then acidified. The oily azoimide was immediately extracted with ether, and ammonia was passed into the cold extract. The crystalline mass which remained on evaporation was dissolved in water and acidified, when azoimide was evolved and the original isopropylmalonic acid separated.

An aqueous solution of the racemic acid and quinine was left in ice, when the salt of the *d*-acid separated as a granular mass. The filtrate contained the salt of the *l*-acid, but, owing to the racemisation, it deposited a further quantity of the salt of the *d*-acid after some weeks, or after it had been warmed. The yield of *d*-acid was therefore much more than 50%. The salt was suspended in chloroform and water, cooled to  $0^\circ$ , and shaken with 0.5*N*-sodium hydroxide. After removing the chloroform extract, the aqueous solution was washed with ether and quickly treated with *N*-hydrochloric acid. It was necessary to carry out these operations with dispatch, since the acid is quickly racemised in alkaline solution. The *d*-isopropylmalonic acid crystallised from water in prisms. The following values for  $[\alpha]_D^{25}$  were observed; in 4.31% alcoholic solution,  $+49.81^\circ$ ,  $4.09\%$ ,  $+49.40^\circ$ ,  $2.02\%$ ,  $+46.52^\circ$ ; in the equivalent quantity of *N*-sodium hydroxide,  $+12.63^\circ$ .

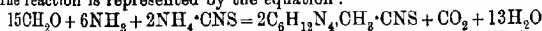
The course of the racemisation in alkaline solution was studied, and the acid was also converted into isopropylmalonic acid by the action of nitrous fumes. The *d*-methyl ester had m. p.  $141^{\circ}$  (corr.) and  $[\alpha]_D^{25}$  in 8.843% alcoholic solution,  $+55.41^{\circ}$ , 9.26%,  $+55.29^{\circ}$ . Change of sign occurred on removing the amido-group. The active amic ester was suspended in ether, mixed with amyl nitrite and a few drops of water, and treated with nitrous fumes. Methyl hydrogen *l*-isopropylmalonate, once distilled, had  $[\alpha]_D^{25} - 0.87^{\circ}$ , or, in the equivalent quantity of *N*-sodium hydroxide,  $[\alpha]_D^{25} + 38.4^{\circ}$ . The undistilled ester was converted, as above, into *l*-isopropylmalonhydrazidic acid which was not obtained optically pure, the highest value being  $[\alpha]_D^{25} - 28.7^{\circ}$ .

In order to reach the desired end, these reactions were carried through quickly, sacrificing the yields with the view of avoiding racemisation. Four grams of methyl *d*-isopropylmalonamate were brought to the above stage, and the crude hydrazide was converted into the azoimide, which was treated with ammonia. The *l*-isopropylmalonamic acid which separated was almost pure, a 4.52% solution in alcohol having  $[\alpha]_D^{25} - 44.40^{\circ}$ .

J. C. W.

**Preparation of Hexamethylenetetramine Camphorates.** FARBERGER VORM. MEISTER, LUCIUS & BRÜNING (Austrian Patent, 63529 & D.R.-P. 270180).—Mono- and di-camphorates of hexamethylenetetramine may be obtained by crystallising a solution of the calculated proportions of the acid and base in an indifferent solvent. They have not the unpleasant effects of hexamethylenetetramine itself, whilst they increase diuresis and render alkaline urine acid. T. H. P.

**Preparation of Hexamethylenetetramine Methyl Thiocyanate.** KARL HEINRICH SCHMITZ (D.R.-P. 270486).—The original process (this vol., i, 20, 503) is altered as follows. Either methylamine salts or ammonium salts or inorganic or organic acids are allowed to act on a mixture of formaldehyde and ammonia or on hexamethylenetetramine; or hexamethylenetetramine salt is heated with or without formaldehyde and the hexamethylenetetramine methyl thiocyanate separated by addition of readily soluble thiocyanates; or methylamine thiocyanate or ammonium thiocyanate or thiocyanic acid is heated either with solutions of formaldehyde and ammonia or with hexamethylenetetramine thiocyanate, in the presence or absence of formaldehyde. The latter may be replaced by its polymerides in all cases. The reaction is represented by the equation:



T. H. P.

**Preparation of a Compound Containing Silicon.** HERMANN WEILAND (D.R.-P. 272338).—When heated in presence of light petroleum in a platinum autoclave for six hours at  $170$ – $180^{\circ}$ , carbamide and silicon tetrachloride interact to form a compound which contains silicon and exhibits the properties of a feeble acid. With sodium hydroxide it gives a soluble sodium salt, which yields the original compound when treated with carbon dioxide. Boiling of the compound with hydrochloric acid results in the separation of gelatinous silicic acid.

T. H. P.

**Preparation of  $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide.** FARBER-FABRIKEN FORM. FRIEDR. BAYER & Co. (D.R.-P. 271682).— $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide, m. p. 115° (compare A., 1911, i, 118), may be prepared by treating  $\alpha$ -bromo- $\alpha$ -ethylbutyryl bromide, in presence of an indifferent solvent, with mercurous cyanate, and subjecting the  $\alpha$ -bromo- $\alpha$ -ethylbutyryl cyanate thus obtained to the action of ammonia:  $2\text{CEt}_3\text{Br}\cdot\text{COBr} + 2\text{HgNCO} = \text{Hg}_2\text{Br}_2 + 2\text{CEt}_3\text{Br}\cdot\text{CO}\cdot\text{NCO}$ , and this  $+ \text{NH}_3 = \text{CEt}_3\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ . T. H. P.

**Complex Cyanides of Quadrivalent Tungsten. III.** OSCAR OLSSON (*Zeitsch. anorg. Chem.*, 1914, 88, 49–73. Compare A., 1913, ii, 328; this vol., i, 504).—The following further cyanides containing quadrivalent tungsten are described:  $\text{Ag}_4\text{W}(\text{CN})_8$ , a yellow, amorphous powder;  $[\text{AgNH}_3]_4\text{W}(\text{CN})_8$ , prepared by dissolving the silver salt in concentrated ammonia, separating on cooling as bright yellow crystals;  $\text{Na}_4\text{W}(\text{CN})_8\cdot 2\cdot 5\text{H}_2\text{O}$ , obtained by the action of sodium chloride on the silver salt as small, yellow crystals;  $(\text{NH}_4)_4\text{W}(\text{CN})_8$ , glistening scales;  $\text{Rb}_4\text{W}(\text{CN})_8\cdot 3\text{H}_2\text{O}$ ;  $\text{Cs}_4\text{W}(\text{CN})_8$ ;  $\text{Ti}_4\text{W}(\text{CN})_8$ ;  $\text{Mg}_2\text{W}(\text{CN})_8\cdot 6\text{H}_2\text{O}$ ;  $\text{Ca}_2\text{W}(\text{CN})_8\cdot 8\text{H}_2\text{O}$ ;  $\text{Sr}_2\text{W}(\text{CN})_8$  or  $9\text{H}_2\text{O}$ ;  $\text{Pb}_2\text{W}(\text{CN})_8\cdot 4\text{H}_2\text{O}$ ;  $\text{Mn}_2\text{W}(\text{CN})_8\cdot 8\text{H}_2\text{O}$ ;  $\text{Cd}_2\text{W}(\text{CN})_8\cdot 8\text{H}_2\text{O}$ ;  $[\text{Cd}(\text{NH}_3)_2]_2\text{W}(\text{CN})_8\cdot 2\text{H}_2\text{O}$ ;  $[\text{Cd}(\text{NH}_3)_3]_2\text{W}(\text{CN})_8\cdot 2\text{H}_2\text{O}$ ;  $\text{ZnW}(\text{CN})_8\cdot 4\text{H}_2\text{O}$ ;  $[\text{Zn}(\text{NH}_3)_2]_2\text{W}(\text{CN})_8$ .

The acid,  $\text{H}_4\text{W}(\text{CN})_8\cdot 6\text{H}_2\text{O}$ , is prepared by treating the silver salt with a small excess of cold dilute hydrochloric acid, and saturating the clear filtrate with hydrogen chloride below 0°. The acid is precipitated quantitatively in yellow needles. It is dried in carbon dioxide, and finally in a desiccator over potassium hydroxide. It is a strong acid, decomposing carbonates and yielding a neutral ammonium salt. Its alcoholic solution yields crystalline compounds with pyridine and quinoline. C. H. D.

**The Technical Methods for the Preparation of Dicyanodiamide from Calcium Cyanamide from the Point of View of Chemical Kinetics.** G. GRUBE and P. NITSCHKE (*Zeitsch. angew. Chem.*, 1914, 27, 368–378).—A new process for the technical preparation of dicyanodiamide from calcium cyanamide is described, in which the calcium hydroxide already present in the solution of the calcium compound is utilised as catalyst. Since the polymerisation proceeds with a maximum velocity when the concentrations of cyanamide and cyanamidion are equal (A., 1914, i, 152; T., 1914, 105, 576), the hydroxide is fractionally neutralised with hydrochloric acid as the reaction proceeds, in order to satisfy this condition. The calcium chloride formed exerts an additional catalytic accelerating influence in the presence of the hydroxide. The new process has been compared by kinetic experiments with the ammonia and zinc cyanamide processes, and it is shown that under proper conditions, the almost quantitative conversion into dicyanodiamide is possible by the lime and ammonia methods, but that side reactions cause considerable loss in the zinc process. Dicyanodiamide formation in neutral solution in the presence of the almost insoluble zinc cyanamide is a heterogeneous catalysis. The reaction-velocity increases at a proportionally greater

rate than the increase in mass of the catalyst, and does not depend on the rate of diffusion, but is determined by a slow chemical action probably consisting, as in the other cases, in the union of cyanamide and cyanamidion.

G. F. M.

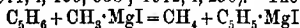
**Phytin.** WOLFGANG HEURNER (*Biochem. Zeitsch.*, 1914, 64, 99—421).—Phytic acid undergoes scission in acid medium at 37° only very slowly, less than 1% being hydrolysed in a day. The hydrolysis is markedly accelerated by light.

S. B. S.

**Hydro-aromatic Substances.** W. H. PERKIN, A. W. CROSSLEY, H. O. FORSTER, H. R. LE SUEUR, and A. MCKENZIE (*Rep. Brit. Assoc.*, 1913, 135—136).—A report of recent work on this subject (T., 1913, 103, 1297, 2179).

C. H. D.

**Derivatives of cyclopentadiene and its Dimeride.** V. GRIGNARD and CH. COUBTOT (*Compt. rend.*, 1914, 158, 1763—1766).—cyclopentadiene resembles indene and fluorene in its behaviour towards magnesium alkyl haloids, giving a magnesium haloid derivative (compare A., 1911, i, 193, 538; 1912, i, 250). The reaction



takes place best in a mixture of ether and light petroleum (60—80°) at 45—50°, when, on cooling at the end of the reaction, the magnesium derivative separates out as a powder. This derivative readily reacts with iodine and bromine or cyanogen bromide or chloride, but the products, in all cases, rapidly undergo dimerisation. Iodine in toluene solution gives a black, insoluble powder, having the composition  $C_{10}H_8I_2$ , but this is evidently a polymeride. Bromine reacts with the magnesiumbromo-derivative in ether at low temperatures to give 3:4:5-tribromo- $\Delta^1$ -cyclopentene, small prisms, m. p. 60°, which is very unstable and is rapidly transformed into the dimeride,  $C_{10}H_{10}Br_2$ , a blackish-brown powder. Attempts to prepare a monobromo-derivative by means of cyanogen bromide only yielded a black powder, which was a mixture of bromo- and cyano-polymerides. Cyanogen chloride yielded the nitrile of bis-cyclopentadienedicarboxylic acid, which on hydrolysis with alcoholic potassium hydroxide yielded the acid (compare Thiele, A., 1901, i, 182). This acid is also obtained directly by the action of dry carbon dioxide on the original magnesium derivative.

With anisaldehyde the magnesium derivative yielded p-methoxy-phenylfulvene,  $\begin{matrix} CH:CH \\ | \\ CH:CH \end{matrix} > C:CH \cdot C_6H_4 \cdot OMe$ , red crystals, m. p. 70°, and with acetone, dimethylfulvene, b. p. 47°/11 mm. (compare Thiele, *loc. cit.*). With benzophenone the alcohol is, however, obtained, being the first known in this series. Diphenylfulvanol is obtained in colourless crystals, m. p. 123—124°, which are very oxidisable and rapidly resinify on attempts to recrystallise them or under the influence of hydrochloric acid or bromine. In sunlight the alcohol is dehydrated, giving diphenylfulvene, red prisms, m. p. 82° (compare Thiele, *loc. cit.*)

W. G.



**Bromination of Benzene and its Homologues, Catalytic Action of Manganese.** L. GAY, F. DUCELLIEZ, and A. RATNAUD (*Compt. rend.*, 1914, 158, 1804—1806. Compare this vol., ii, 273).—Bromine attacks benzene at 75° in the presence of manganese, but only at 90° in the absence of the metal. Working under similar conditions of temperature, manganese is shown to have a marked catalytic influence. The ratio of recovered benzene to brominated benzene is 8 : 9 in the presence of manganese and 10 : 3 in its absence. Manganese exerts a similar catalytic influence on the bromination of toluene and xylene in the cold, but on working at 80° for toluene and 50° for xylene this action is masked, better results being obtained without the manganese. In no case is the metal attacked. W.G.

**Some Hydrogenations by means of Sodammonium Hydrocarbons.** P. LEBEAU and M. PICON (*Compt. rend.*, 1914, 159, 70—72).—Using sodium in liquid ammonia under the conditions given for tetrahydronaphthalene (compare this vol., i, 825), the authors have prepared hydrides of a number of hydrocarbons, all of which have been previously described, namely: tetrahydroacenaphthene (compare Bamberger and Lotter, A., 1888, 292), dihydroanthracene (*loc. cit.*), tetrahydrophenanthrene (compare Breteau, A., 1911, i, 625), tetrahydrodiphenyl (*loc. cit.*), and dihydrostilbene. The other product of the reaction is in all cases sodamide. Attempts to hydrogenate amylene, benzene, toluene, cymene, terpinene, terpinolene, carvene, terebene,  $\alpha$ -pinene and menthene by this method were unsuccessful. Fluorene and indene instead of undergoing hydrogenation gave sodium derivatives. W. G.

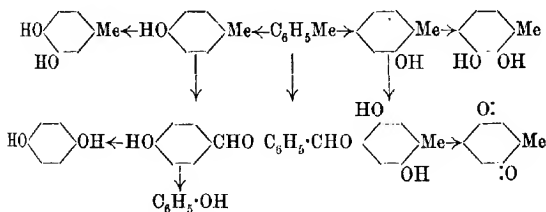
**The Electrochemical Oxidation of Aromatic Hydrocarbons and Phenols.** FR. FICHTER and ROBERT STOCKER (*Ber.*, 1914, 47, 2003—2019. Compare Fichter, A., 1913, i, 1316).—By submitting phenol in a feebly acid sulphate solution to an alternating current between platinum electrodes, Drechsel (A., 1884, 1136; 1888, 1276) was able to produce a mixture of substances which he classified into oxidation products, namely, quinol, catechol, *p*-diphenol, oxalic and formic acids, reduction products, namely, cyclohexanone and succinic acid, and dehydration products of which the only example was phenyl hydrogen sulphate. The authors desired to reproduce these results with a direct current; they discovered that under electrolytic oxidation phenol and benzene yield the same end-products, so that the examination of the behaviour towards electrolytic oxidation was extended to certain homologues and substituted derivatives of phenol and benzene. The substances were generally treated in suspension in 2*N*-sulphuric acid.

It is found that electrolytic oxidation of benzene and its derivatives effects nuclear hydroxylation; the first product from benzene is phenol, which is too easily oxidised to be isolated, and is further converted into catechol and quinol. The former is difficult to detect on account of its passing readily into higher oxidation products, and the isolation of appreciable quantities by Drechsel is attributed to the alterna-

tion of the current tending to check the increase in the oxidation potential of the electrodes. The latter substance passes by oxidation into the relatively stable *p*-benzoquinone, which, if the anode and cathode are separated, together with its degradation product maleic acid, forms the main part of the final product, whilst if no diaphragm is used cathodic reduction reconverts some of the *p*-benzoquinone into quinol. Contrary to the views of Kempf (A., 1907, i, 63; 1906, ii, 24, 25), who regards lead dioxide as the chief agent in electrochemical oxidation at a lead anode, it is found that the same products are obtained whether platinum, lead or graphite electrodes are used. The hypothesis that electrolytic oxidation in sulphuric acid solution depends on the intermediate formation of persulphuric acid is also untenable because the result is qualitatively the same when aqueous phosphoric or perchloric acid is used for the suspension, and it is unlikely that genuine "per-acids" are produced under such conditions from either of these acids.

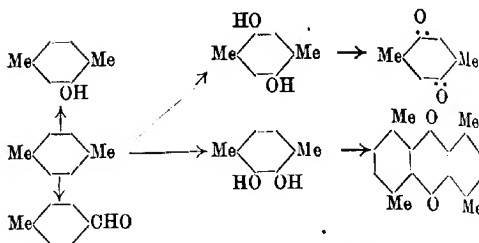
Attention is drawn, by the citation of examples, to the remarkable frequency with which electrolytic oxidation and treatment with hydrogen peroxide yield similar results, and the suggestion is made that an important point of analogy between these agents is the absence of formation of lower oxides which may exert catalytic influence on the oxidation process.

Electrochemical oxidation of toluene in suspension in dilute sulphuric acid was found to give rise to toluquinone, quinol and phenol together with a smaller quantity of benzaldehyde (compare Law and Perkin, T., 1907, 91, 258). The fact that the aromatic nucleus is attacked in preference to the side-chain is in accord with the results of electrochemical chlorination of toluene (compare Cohen, Dawson and Crosland, T., 1905, 87, 1034). In explanation of the above behaviour of toluene the following scheme is suggested:—



in which the final members not included in the experimental products undergo disruptive oxidation. This view of the process is confirmed by examination of the behaviour of *o*- and *p*-cresol on electrolytic oxidation.

*p*-Xylene, in suspension in dilute sulphuric acid, on treatment at a lead dioxide anode, gave in addition to a small quantity of *p*-tolualdehyde (compare Law and Perkin, *loc. cit.*), *p*-xyloquinol and a substance, silky needles, m. p. 161°, probably *p*-xylylene dioxide. The changes are represented by the scheme



Nitrobenzene proved very resistant to anodic oxidation, and the only isolable oxidation product was maleic acid, which was also obtained with *o*- and *m*-nitrophenols; *p*-nitrophenol was completely destroyed. Trichlorophenol gave an unsatisfactory yield of 2:6-dichloroquinol, and thymol gave thymoquinol, together with a mixture of difficultly crystallisable substances from which dithymol could be separated.

The last product is interesting as corresponding with the diphenol obtained by Drechsel, but which the authors have been unable to produce by the electrolytic oxidation of phenol; with the possible exception of this, all the oxidation products named by Drechsel are formed in the electrolytic oxidation of phenol with a direct current. The production of his reduction products was probably to a large extent due to the formation of platinum black on his electrodes; under these conditions, maleic acid would be easily reduced to succinic, and phenol would give cyclohexanol, which by subsequent oxidation could pass into cyclohexanone.

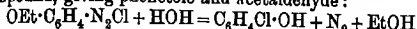
The authors are, however, unable to confirm the formation of phenyl hydrogen sulphate and bring evidence indicating that the substance described by Drechsel was in reality quinolsulphuric acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_3\text{H}$ .  
D. F. T.

**Separation of the Hydrochlorides of Primary Aromatic Amines and their Derivatives from the Products of Reaction of the Corresponding Nitro-, Nitroamino-, Nitroso-, Azoxy-, Azo-, Hydroxyazo-, and Amin-azo-compounds with Iron and Hydrochloric Acid.** HIRSCH POMERANZ (D.R.-P. 269542).—When the proportion of iron and the proportion and concentration of the hydrochloric acid employed in this reduction are so chosen that the resultant mixture of ferrous chloride, water, free hydrochloric acid, and hydrochloride of the base is just saturated in the cold with respect to ferrous chloride, the hydrochloride of the amine separates almost quantitatively from the liquid. Loss due to oxidation of the liberated amine is thus avoided.  
T. H. P.

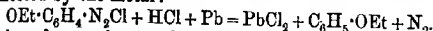
**Diazotisation of Phenetidines.** TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1914, 235—249).—It has been shown by Swarts (*A.*, 1913, i, 842) that considerable quantities of phenetole are formed in addition to fluorophenetoles when *o*- and *p*-phenetidine are diazotised in the presence of hydrofluoric acid and the diazo-compound is subsequently

decomposed; the relative amount of fluoro-compound is greatest when platinum, least when leaden vessels are employed. The reaction has been further investigated by the author, who, however, has generally used solutions of the bases in hydrochloric instead of hydrofluoric acid, since the reaction is found to proceed in an analogous manner in the two cases.

A solution of *o*-phenetidine in hydrochloric acid is diazotised by means of a concentrated solution of sodium nitrite, and the product decomposed by boiling the solution. In these circumstances, decomposition occurs slowly with the production of much resin, from which a definite product cannot be isolated. The portion volatile with steam and insoluble in sodium hydroxide contains phenetole (43%) and *o*-chlorophenetole (47%); the soluble portion consists mainly of the ethyl ether of catechol. In addition, ethyl chloride and acetaldehyde are formed. The formation of the latter is attributed to the hydrolysis of the ethoxy-group with the formation of alcohol, which then reduces the diazo-compound, giving phenetole and acetaldehyde:



and  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl} + \text{EtOH} = \text{C}_6\text{H}_4\text{OEt} + \text{N}_2 + \text{C}_2\text{H}_5\text{O} + \text{HCl}$ . The relative quantities of aldehyde and phenetole are shown to be approximately those required by the equation. In the presence of metallic lead, the proportion of phenetole is increased to 78%, but the quantity of acetaldehyde formed is insignificant, reduction of the diazo-compound being affected by the metal:



A series of experiments has been performed with the object of ascertaining the most favourable conditions for diazotising *o*-phenetidine in the presence of hydrofluoric acid, for which purpose an initial concentration of 55% acid is found best. Subsequent decomposition of the diazo-compound occurs with extreme slowness, but attempts to hasten it by adding the solution to a boiling concentrated solution of potassium fluoride in hydrofluoric acid, or by the use of manganese or antimony fluorides, do not yield better results.

*p*-Phenetidine when diazotised in hydrochloric acid solution and subsequently decomposed behaves in a manner very similar to that of the *o*-compound, except that the auto-reduction, as well as the action of lead, is relatively of less importance.

Elimination of the ethoxy-group appears to take place from the diazo-compound and not from the free base, since phenetole does not yield alcohol when boiled with hydrochloric acid for four hours, and only gives traces of alcohol when hydrofluoric acid is used: analogous results are obtained with *o*-phenetidine, which, however, yields a small quantity of *o*-aminophenol when treated with hydrofluoric acid.

Aldehyde is not formed when aniline is diazotised and the product decomposed in the presence of a small proportion of alcohol. A similar experiment in which *o*-phenetidine is diazotised in the presence of the calculated quantity of hydrochloric acid, and the product decomposed after addition of so much alcohol that its concentration is approximately 10%, shows the formation of considerable amounts of

acetaldehyde: the latter is also produced, but in less quantity, without the addition of extraneous alcohol.

H. W.

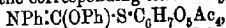
**The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives.** F. S. KIPPING, K. J. P. ORTON, S. RUHEMANN, and J. T. HEWITT [with W. H. GRAY] (*Rep. Brit. Assoc.*, 1913, 136—141).

—The behaviour of acetylchloroaminobenzene, which has been previously examined in solutions containing acetic acid, has now been examined in pure aqueous solution. The rate of change in pure water is very slow, and small concentrations of acids produce only a small acceleration. Hydrolysis takes place, followed by reduction of the hypochlorous acid. The transformation of chloroamine into chloroanilides is quite subsidiary. With concentrations of hydrogen chloride above *N*/10, chlorine is not hydrolysed, and the formation of chloroanilide is the principal reaction. Other acids do not produce the same effect. The views as to the mechanism of these reactions put forward in previous papers are confirmed (compare Rivett, A., 1913, ii, 202).

C. H. D.

**Thiocarbimides. VI. The Addition of Phenol to Thiocarbimides.** WILHELM SCHNEIDER and FRITZ WREDE (*Ber.*, 1914, 47, 2038—2043).—Some uncertainty exists as to whether phenols can condense with thiocarbimides with the formation of thiourethanes (compare Orndorff and Richmond, A., 1900, i, 157; Eckenroth and Kock, A., 1894, i, 408). By working with lower temperatures than those previously applied, the authors have been able to prepare additive compounds of phenol with phenylthiocarbimide and with allylthiocarbimide.

An equimolecular mixture of phenol and phenylthiocarbimide was kept at 80° for a day and then at the ordinary temperature for several days; after the addition of alcohol and cooling, an aqueous-alcoholic ammoniacal solution of silver nitrate was added, when the *phenyl silver phenyliminothiocarbonate*,  $\text{NPh}\cdot\text{C}(\text{SAg})\cdot\text{OPh}$ , rhombic, bronze-yellow crystals, m. p. 186°, separated. A similar result is obtained if the mixture of phenol and phenylthiocarbimide is merely kept at the ordinary temperature for two months. When treated with acetobromoglucose in chloroform solution the silver salt was converted, in very poor yield, into the corresponding *tetra-acetylglucoside*,



colourless needles, m. p. 169°. The action of hydrogen sulphide on a chloroform solution of the silver salt liberated phenyl phenylthiocarbamate,  $\text{NHPh}\cdot\text{CS}\cdot\text{OPh}$ , colourless needles, m. p. 142° (compare Rivier, A., 1906, i, 948), of feeble odour, which in contact with water undergoes gradual resolution into phenol and phenylthiocarbimide.

By a similar process to the preceding, but using allylthiocarbimide the *silver derivative*, yellowish-green rhombs, decomp. above 140°, or phenylallylthiocarbamate was obtained. This on treatment with hydrogen sulphide in chloroform solution gave *phenyl allylthiocarbamate*,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{OPh}$ , leaflets or needles, m. p. 51°, which is rather more stable than phenyl phenylthiocarbamate. When heated with alcohol

and excess of ethyl iodide, the silver derivative was converted into *O*-phenyl-*S*-ethyl allyliminothiocarbonates,  $C_6H_5 \cdot N : C(SET) \cdot OPh$ , a colourless liquid of not unpleasant odour, b. p. 150—160°/20 mm. No crystalline tetra-acetylglucoside was obtainable by the action of acetobromoglucose.

D. F. T.

**Oxidation of Phenol.** H. WIEHELHAUS (*Ber.*, 1914, 47, 2261).—Commenting on a statement recently made by Pummerer and Frankfurter, to the effect that nothing is known about the oxidation of phenol, the author refers to the production of phenoquinone (A., 1872, 482).

J. C. W.

**Catalytic Reactions at High Temperatures and Pressures.**  
XXXIV. **Hydrogenation of Monohydric Phenols.** V. IPATIEV and LUGOVOI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 470—475).—The slowness with which quinol is reduced by hydrogen at high pressure in presence of nickel oxide or reduced nickel and the small yields of quinitol occasioned by the loss of the elements of water and by the partial resinification of the quinol itself have led to the use of simple ethers of phenols in the hope that the methoxy-group would not be eliminated so easily and that resinification would be avoided. Preliminary experiments with the ethers of various phenols showed that such expectation is fulfilled only incompletely and that, although better yields of the normal hydrogenated products are obtained, these are accompanied by secondary products often difficult to remove (this vol., i, 38).

When guaiacol is heated for twelve to fifteen hours at 220—240° with one-tenth of its weight of nickel oxide in an atmosphere of hydrogen at 100 atmospheres, it yields hexahydroguaiacol [2-methoxycyclohexanol] mixed with a little cyclohexane and about 50% of cyclohexyl alcohol. By treatment of the products with alumina and cupric oxide at 250° in an atmosphere of hydrogen at 50 atmospheres, the cyclohexyl alcohol is converted into cyclohexene and may be separated from the 2-methoxycyclohexanol, which is transformed into hexahydrocatechol [cyclohexane-1 : 2-diol].

Hydrogenation of anisole under a pressure of 100 atmospheres in presence of nickel oxide at 240° for twenty-four hours yields cyclohexene, hexahydroanisole [methoxycyclohexane] (about 50%) and cyclohexyl alcohol.

Similarly, the diethyl ether of catechol yields about 50% of the normal hexahydro-derivative,  $C_6H_{10}(OEt)_2$ , apparently in the *cis*- and *trans*-modifications, b. p. 180—190°, and b. p. 190—200°,  $D_{20}^{20}$  0.8997 respectively; the remainder is converted into cyclohexene. With the dimethyl ether of resorcinol, besides the normal product, a considerable proportion of cyclohexane seems to be formed. The dimethyl ether of quinol gives the normal hydrogenated product, together with a large proportion of methoxycyclohexane.

T. H. P.

**The Allylcyclohexanols and Methylallylcyclohexanols, Propyl- and Methylpropyl-cyclohexanones, and cycloHexanols.** R. JANUERT (*Compt. rend.*, 1914, 159, 75—80).—The allyl- and methylallyl-cyclohexanones already described (compare this vol., i, 969)

on reduction with sodium in absolute alcohol yield the corresponding cyclohexanols, and on hydrogenation with active nickel in alcohol at 60° (compare Brochet, this vol., i, 645) the corresponding propylcyclohexanones which have been reduced to the cyclohexanols. The following compounds are described.

1 : 1 : 3 : 3-Tetra-allylcyclohexan-2-ol, a viscous liquid, b. p. 184—185°/24 mm. (corr.), not giving a phenylurethane (compare Haller, A., 1913, i, 630). 1-Methyl-3-allylcyclohexan-2-ol, a mobile liquid, with an odour of menthol, b. p. 105°/15 mm. (corr.), giving a phenylurethane, a very viscous liquid. 1-Methyl-1 : 3 : 3-triallylcyclohexan-2-ol, a very viscous liquid, b. p. 160—161°/15 mm. (corr.), not giving a phenylurethane. 1-Methyl-4-allylcyclohexan-3-ol, a mobile liquid with an odour of menthol, b. p. 110—112°/19 mm., giving a phenylurethane, a very viscous liquid. 1-Methyl-2 : 2 : 4 : 4-tetra-allylcyclohexan-3-ol, a mobile liquid, b. p. 192—193°/21 mm., does not give a phenylurethane. 1-Methyl-3-allylcyclohexan-4-ol, a slightly viscous liquid, b. p. 108°/17 mm. (corr.), giving a phenylurethane, slender needles, m. p. 98—99°. 1-Methyl-3 : 3 : 5 : 5-tetra-allylcyclohexan-4-ol, a slightly viscous liquid, b. p. 173—174°/17 mm. (corr.), does not give a phenylurethane.

1 : 1 : 3 : 3-Tetrapropylcyclohexan-2-one, prisms, m. p. 43°, does not give an oxime, but on reduction gives the corresponding alcohol, a very viscous liquid, b. p. 188°/25 mm. (corr.), not giving a phenylurethane. 1-Methyl-3-propylcyclohexan-2-one is a colourless, mobile liquid with an odour of menthone, b. p. 213·5°/765 mm. (corr.), gives an oxime, m. p. 70°, and on reduction the alcohol, a mobile liquid, b. p. 115°/25 mm., giving a phenylurethane, a very viscous liquid. 1-Methyl-1 : 3 : 3-tripropylcyclohexan-2-one is a colourless, mobile liquid, b. p. 152°/14 mm. (corr.), not giving an oxime, but yielding an alcohol, a very viscous liquid, b. p. 173°/27 mm., which does not give a phenylurethane. 1-Methyl-4-propylcyclohexan-3-one, a colourless, mobile liquid with an odour of menthone, b. p. 217°/765 mm. (corr.), gives an oxime, needles, m. p. 78—82°; and the corresponding alcohol, a mobile liquid, b. p. 107—108°/17 mm., giving a phenylurethane, a very viscous liquid. 1-Methyl-2 : 2 : 4 : 4-tetrapropylcyclohexan-3-one, a colourless, very viscous liquid, b. p. 181°/19 mm. (corr.), does not give an oxime, but is reduced to the alcohol, a viscous liquid, b. p. 185°/18 mm. (corr.), which does not give a phenylurethane. 1-Methyl-3-propylcyclohexan-4-one, a colourless, mobile liquid, with an odour of menthone, b. p. 217°/750 mm. (corr.), giving an oxime, slender needles, m. p. 67—68°, and on reduction the alcohol, a slightly viscous liquid, b. p. 112°/18 mm. (corr.), which yields a phenylurethane, a very viscous liquid. 1-Methyl-3 : 3 : 5 : 5-tetrapropylcyclohexan-4-one, prisms, m. p. 49°, not giving an oxime, but on reduction the alcohol, a very viscous liquid, b. p. 178°/16 mm. (corr.), not giving a phenylurethane.

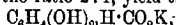
The hydrogenation of the allylcyclohexanones thus gives a ready method of preparing the propylcyclohexanones, which cannot be obtained by direct alkylation with propyl iodide and sodamide. In this hydrogenation the various samples of active nickel prepared appeared to possess a selective action as catalysts, in that they effected the hydrogenation of some compounds and not of others. In the case

of the polyallyl ketones certain nickels provoked the rapid saturation of one or two double linkings, and only a slower saturation of the others, whilst with other nickels no such difference was observable.

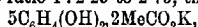
W. G.

**Compounds of Catechol with Alkaline Salts of Carboxylic Acids.** R. F. WEINLAND and WILHELM DENZEL (*Ber.*, 1914, 47, 2244—2252).—It was recently found that catechol forms complex compounds with its own alkali salts (this vol., i, 525). In the present paper, similar compounds of catechol with the sodium and potassium salts of typical carboxylic acids are described. They cannot be explained by Pfeiffer's views (this vol., i, 834), for, in some cases, the partial valency of a single carbonyl group would have to satisfy several hydroxyl groups. Since catechol does not combine with the free acids, the metallic atom must provide the connecting links, and it is therefore assumed that the substances are like co-ordinated aquo-compounds, in which one molecule of catechol plays the part of two molecules of water.

A solution containing equimolecular proportions of sodium formate and catechol, when left over sulphuric acid, deposits the compound,  $C_6H_4(OH)_2 \cdot H \cdot CO_2Na \cdot H_2O$ , in colourless needles and tablets, which are feebly alkaline in concentrated solution. A solution containing sodium formate and catechol in the ratio 1 : 1.75 deposits the compound,  $2C_6H_4(OH)_2 \cdot H \cdot CO_2Na$ , in needles or four-sided columns. Potassium formate and catechol in the ratio 2 : 1, yield the compound,

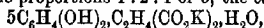


very large, thick, rectangular tablets; in the ratio 1 : 1, the compound,  $7C_6H_4(OH)_2 \cdot 4H \cdot CO_2K \cdot H_2O$ , long, thin tablets; and in the ratio 1 : 2.75, the compound,  $7C_6H_4(OH)_2 \cdot 2H \cdot CO_2K$ , large, transparent crystals. A 96% alcoholic solution of potassium acetate and catechol in the ratio 1 : 1 deposits the compound,  $C_6H_4(OH)_2 \cdot MeCO_2K$ , long, thin tablets, and in the ratio 1 : 2.25 to 2.75, the compound,

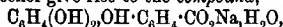


colourless octahedra.

Solutions containing succinic acid, potassium hydroxide and catechol in the proportions 1 : 1.1 or 2 or 3, or 1 : 1.5 : 2, deposit the compound,  $2C_6H_4(OH)_2 \cdot CO_2H \cdot C_2H_4 \cdot CO_2K$ , in variously shaped, massive crystals, the solutions of which are strongly acid; in the proportions 1 : 2 : 1 or 3, the compound,  $3C_6H_4(OH)_2 \cdot C_2H_4(CO_2K)_2 \cdot 4.5H_2O$ , which is feebly alkaline; and in the proportions 1 : 2 : 4 or 5, the compound,



irregular, hexagonal columns. Equimolecular proportions of sodium salicylate and catechol give rise to the compound,



which is faintly acid in reaction and forms very slender needles.

J. C. W.

**Synthesis of Natural Inositol.** HEINRICH WIELAND and ROBERT S. WISHART (*Ber.*, 1914, 47, 2082—2085).—The authors have succeeded in reducing hexahydroxybenzene to an inositol, which, of the seven possible isomerides, happens to be the one which occurs most commonly in nature.



The purest hexahydroxybenzene, prepared from carbon monoxide by Nietzki and Benckiser's method, was suspended in water and shaken with palladium black, quite free from hydrochloric acid, in an atmosphere of hydrogen, at 50—55°, until saturation took place. The inositol obtained on evaporation of the clear filtrate was completely identified with the natural substance and also converted into the hexacetate.

J. C. W.

**Nitration of the Acyl Derivatives of *m*-Aminophenol.** [Correction.] FRÉDÉRIC REVERDIN (*Ber.*, 1914, 47, 2216—2218).—In a recent paper (this vol., i, 166) the author reported that he could not confirm Meldola's statement that the product of the action of nitric acid on diacetyl-*m*-aminophenol is a mixture of 4- and 6-nitro-3-acetylaminophenols (compare T., 1914, 105, 977, footnote). Having now learnt from Meldola the exact experimental details, he finds that the above statement is correct.

Reverdin also described, as the sole product of the nitration at low temperatures, 6-nitrodiaetyl-*m*-aminophenol. He has now found that, even at -7°, both isomerides are formed, accompanied by the monoacetyl derivatives, that is, the free phenols. The above compound, therefore, required digestion with cold sodium carbonate solution in order to remove traces of the corresponding phenol. The m. p. is now given as 149° and not 113°, and the free 6-nitro-3-acetylaminophenol obtained from it is found to have the correct m. p. 220—221°, and not 200°.

J. C. W.

**The Mechanism of the Action of Magnesium Alkyl Haloids on Esters.** G. STADNIKOV (*Ber.*, 1914, 47, 2132—2142).—In extension of his investigations of the oxonium compounds produced from magnesium alkyl haloids and ethers (*A.*, 1913, i, 1183, 1335) the author finds that esters and magnesium alkyl haloids form similar oxonium compounds and that the latter possess the constitution suggested by Grignard, namely,  $R \cdot CO \cdot OR' \cdot MgX$ , for the possible decompositions into  $R \cdot COR' + OR' \cdot MgX$ ,  $R \cdot CO_2 \cdot MgX + R'R''$  and  $R \cdot CO_2 \cdot MgX + \frac{1}{2}R'R' + \frac{1}{2}R'R''$  respectively, can in some cases be experimentally realised.

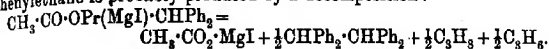
Benzhydryl acetate, b. p. 171—172°/12 mm., prepared by the action of diphenylbromourethane on potassium acetate in acetic acid solution, on treatment with an equimolecular proportion of magnesium ethyl iodide in the cold, gave a colourless precipitate of an oxonium complex which on treatment with water regenerated almost the whole of the ester unchanged.

When benzhydryl acetate was treated in ethereal solution with magnesium ethyl iodide, the former being in excess, the mixture on boiling gave a certain quantity of ethane with a smaller quantity of ethylene, and on subsequent addition of water, besides a further small quantity of these gases, methyldiethylcarbinol, b. p. 122—125°/750 mm., and *s*-tetraphenyldimethyl ether, m. p. 108—109°, were obtained together with unaltered benzhydryl acetate. The result indicated a reaction between one molecule of ester and two of organo-

magnesium compound, the first point of attack in the ester being, not the carbonyl group, but the alkyloxy-group.

An excess of benzhydryl acetate and magnesium isocamyl iodide under similar treatment produced methylidisoamylcarbinol, b. p. 12—114°/14 mm., benzhydrol and unaltered benzhydryl acetate, the reaction having proceeded in a normal manner.

Under similar conditions, benzhydryl acetate and magnesium propyl iodide gave during the heating some propane with less propylene and a little hydrogen, whilst on subsequent treatment with water, the mixture yielded tetraphenylethane, m. p. 208°, *s*-tetraphenyldimethyl ether, methylpropylcarbinol, b. p. 159—161°/755 mm., an oily substance, b. p. 147—153°, and benzhydrol. The formation of methylpropylcarbinol arises from the normal manner of reaction, whilst the tetraphenylethane is probably produced by a decomposition:



Benzhydryl acetate and magnesium butyl iodide in ethereal solution gave some butane and butylene during the heating and *s*-tetraphenylethane, methylbutylcarbinol, b. p. 84—85°/10 mm., benzhydrol and a substance, b. p. 150—160°/12 mm., on subsequent treatment with water. The formation of the tetraphenylethane is attributed to a decomposition corresponding with the last of the three types of decomposition mentioned above.

With magnesium phenyl bromide, benzhydryl acetate gave *s*-tetraphenyldimethyl ether, a substance, b. p. 130—145°/9 mm., and *aa\beta*-triphenylpropylene,  $\text{CPhMe}\cdot\text{CPh}_2$ , m. p. 121—122°, the formation of the last named being ascribed to a subsequent action of the organo-magnesium compound on the *as*-diphenylacetone produced from the oxonium additive compound by a primary decomposition belonging to the first of the above three types.

Benzyl benzoate and magnesium phenyl bromide reacted in ethereal solution, giving benzoic acid, phenol, benzyl alcohol, triphenylcarbinol, m. p. 164—165°, and triphenylethylene, m. p. 72—73° (compare Staudinger and Kon, A., 1911, i, 876). Again, a decomposition of the primary oxonium compound has probably occurred according to the first of the above possibilities, the resulting phenyl benzyl ketone giving triphenylethylene on reaction with more organo-magnesium compounds, followed by dehydration of the primarily resulting *aa\beta*-triphenylethyl alcohol.

D. F. T.

**Diphenylnitric Oxide, a New Organic Radicle with Quadri-valent Nitrogen.** HEINRICH WIELAND and MORITZ OFFENBÄCHER (Ber., 1914, 47, 2111—2115).—Diphenylhydroxylamine has been oxidised to the compound,  $\text{Ph}_2\text{N}\cdot\text{O}$ , which bears a great resemblance to nitrogen peroxide, with regard both to its colour and its reactivity.

Better results in the preparation of diphenylhydroxylamine are obtained by decomposing the mixture of magnesium phenyl bromide and nitrosobenzene at once, and not after some hours (A., 1912, i, 253). An ethereal solution of the compound is shaken with dry silver oxide at 0°, when a deep red colour develops. After a few minutes, the mixture is dehydrated by sodium sulphate, filtered, diluted with

petroleum, and plunged into a mixture of ether and solid carbon dioxide. About 75% of the theoretical quantity of *diphenylnitric oxide* separates after a short time, in sparkling, deep red needles, m. p. 62° (decomp.), which cannot be kept for more than a day. The compound is uni-molecular in benzene, and is, apparently, unassociated at very low temperatures. It liberates iodine from potassium iodide and changes thereby into diphenylamine, quantitatively, and it decolorises bromine with the formation of tetrabromodiphenylamine. Concentrated acids react explosively, sulphuric acid giving a deep blue solution. The dark red solutions are decolorised at once by nitric oxide or triphenylmethyl.

The discovery of this compound confirms the assumption that the red, highly reactive substance, porphyrexide (Piloty and Schwerin, A., 1901, i, 517, 583), also contains quadrivalent nitrogen, and it may also strengthen the evidence against a ring-formula, with bivalent nitrogen for nitrogen peroxide.

J. C. W.

**Oxonium Compounds. IV.** G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 459—469).—Tschelincev and Pavlov's criticisms (A., 1913, i, 461) are refuted and Stadnikov and Kuzmina-Aron's conclusions (A., 1912, i, 971) confirmed by the results of further experiments.

T. H. P.

**Arylsulphuric Acids.** EMIL CZAPEK (*Monatsh.*, 1914, 35, 635—642).—Potassium phenyl sulphate is readily obtained by the following modification of Baumann's method. A mixture of phenol with 60% of potassium hydroxide and 80% of water is treated at 60—63° with finely powdered potassium pyrosulphate (125%) at such a rate that the temperature is maintained between 60° and 70°. The mixture is stirred mechanically for eight to ten hours at this temperature, and is then cooled and repeatedly extracted with boiling 96% alcohol to remove the potassium phenyl sulphate. *Potassium  $\alpha$ -naphthyl sulphate*, m. p. 182°, apparently rhombic, pearly leaflets, is prepared in a similar manner at 40—45°.

Arylsulphuric acids are obtained easily, generally, and in good yields by the following modification of Verley's method. Phenol (50 parts), dissolved in a little pyridine or chloroform, is allowed to flow into a well-stirred, cold mixture of chlorosulphonic acid (60 parts), chloroform (500 parts), and pyridine (100 parts), the temperature being kept below 45°. When the pyridine chlorosulphonate has almost disappeared, the chloroform is removed below 45° in a vacuum, concentrated aqueous potassium hydroxide (80 parts) is added, the pyridine is distilled in a vacuum, and the residue is extracted, firstly with petroleum to remove impurities, and then with boiling alcohol to dissolve the potassium phenylsulphate. Substantially in the same manner have been prepared *potassium menthyl sulphate*, m. p. 190—195°, colourless, silky needles, *potassium bornyl sulphate*, pearly needles or leaflets, *potassium quinolyl 8-sulphate*, slender needles, and *potassium quinolyl 2-sulphate*.

The preceding salts do not react with ferric chloride and are converted into the corresponding sulphonic acids by heating at 150—200°. C. S.

**Cadmium Salicylate.** W. GECHNER DE CONINCK (*Bull. Soc. chim.*, 1914, [iv], 15, 608—609).—Cadmium carbonate and salicylic acid interact to form cadmium salicylate, which crystallises in plates or needles as monohydrate. In the presence of water at 76—77° it undergoes partial decomposition with the liberation of salicylic acid; at 165—167° it evolves carbon dioxide, with the production of phenol and probably a basic salt,  $C_6H_4 \begin{smallmatrix} \diagup CO_2 \\ \diagdown O \end{smallmatrix} Cd$ ; above 170° it chars.

A. J. W.

**The Hydroxybenzoates.** W. GECHNER DE CONINCK (*Rev. Gén. Chim. pure appl.*, 1914, 17, 72—75. Compare A., 1907, i, 532, 621, 1042).—A study of calcium salicylate,  $[C_6H_4(OH) \cdot CO_2]_2Ca \cdot 2H_2O$ . The salt is soluble to the extent of approximately 28.46 and 15.50 grams in water and in alcohol at 15.5 and 16.7° respectively. When solutions in these solvents are distilled, no decomposition of the salt occurs, although after heating with water the salt can be obtained in the form of a *trihydrate*. The aqueous solutions acquire a rose-coloured and then a yellow tint on exposure to light. Methyl alcohol is an excellent solvent for the salt.

On heating at 100—115°, the salt loses  $1H_2O$ , and at higher temperatures undergoes decomposition, giving carbon dioxide, phenol, and a so-called basic calcium salicylate,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CO_2 \end{smallmatrix} Ca$ ; the evolution of carbon dioxide commences at 243—244°.

Distillation of a mixture of the salt with such acids as formic, acetic, propionic, gallic, mucic, benzoic, vanillic, and *m*- and *p*-hydroxybenzoic, water also having been added, causes liberation of salicylic acid; hydrogen sulphide, the *o*- and *p*-nitrophenols and picramic acid do not effect such displacement.

After heating in a closed tube for fifteen hours at 215°, no indications of isomeric change with the formation of *m*- or *p*-hydroxybenzoic acid were observable. D. F. T.

**Preparation of Sodium Acetylsalicylate** [*o*-Acetoxybenzoate]. JOHANN A. WELFING (D.R.-P. 270326).—*o*-Acetoxybenzoic acid is converted into its sodium salt by treating it, in a powdered dry condition, with the equivalent proportion of anhydrous sodium carbonate in the presence of ethyl acetate. T. H. P.

***ω*-Bromotoluic Acids.** I. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 508—511).—*ω*-Bromo-*p*-toluic acid,  $CH_2Br \cdot C_6H_4 \cdot CO_2H$ , obtained by the interaction of bromine and *p*-toluic acid dissolved in bromoform, crystallises in plates, *m. p.* 223°, having a vitreous lustre and an irritant action on the mucous membrane; on oxidation with permanganate, it yields terephthalic acid. The *chloro-anhydride*, *m. p.* 56°, which has an irritating odour, yields the *methyl ester*,  $C_6H_4O_2Br$ .

vitreous needles, m. p. 53—53.5°, b. p. 160—161°/17 mm., when treated with methyl alcohol. The action of ethyl alcohol and sulphuric acid on the free acid yields *ethyl o-ethoxy-p-toluate*,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , b. p. 277.5—278.5°, 163—165°/18 mm.; the corresponding acid,  $\text{C}_9\text{H}_9\text{O}_3$ , m. p. 78—79°, which gives terephthalic and acetic acids on oxidation, and also its silver salt were prepared and analysed.

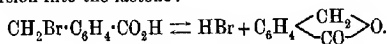
*o-Bromo-o-toluic acid*,  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , prepared by the action of hydrobromic acid on phthalide, forms prismatic crystals, m. p. 147°; its methyl ester,  $\text{C}_9\text{H}_9\text{O}_2\text{Br}$ , is a viscous liquid,  $D_4^{20}$  1.4136,  $D_4^{15}$  1.3882, which emits a vapour having a marked irritant effect on the eyes and mucous membrane and decomposes with the formation of phthalide on distillation under diminished pressure.

T. H. P.

*o-Bromotoluic Acids*. II. J. S. ZALKIND and A. S. SEMESOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 512—517. Compare preceding abstract).—*o-Bromo-m-toluic acid*,  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , prepared by brominating *m*-toluic acid in bromoform solution, forms white crystals, m. p. 151—152°, and emits a vapour which produces violent itching of the skin and mucous membrane; on oxidation with permanganate, it yields isophthalic acid. Its ethyl ester,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ , is an oily liquid, b. p. 160—161°/10 mm.

Since *o*-bromo-*m*- and -*p*-toluic acids readily exchange their bromine for hydroxyl or ethoxyl, and the *o*-acid gives up hydrogen bromide to form phthalide, the authors have investigated the influence of the carboxyl group on the mobility of the bromine atom. With the *p*- and *m*-acids, the action of water proceeds according to the equation  $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O} = \text{HBr} + \text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , and at 50° when a large excess of water is employed, the values of  $k$  calculated from the formula for unimolecular reactions are virtually constant.

In the case of the *o*-acid, the action of water is a reversible reaction, which leads to a chemical equilibrium, two-thirds of the acid undergoing conversion into the lactone:



At 0°, the values of  $k = 1/t \cdot \log[(2-x)/(2-3x)]$  exhibit a gradual but marked diminution, apparently owing to the influence of the increasing number of hydrogen ions on the velocity of the reaction. In the action of water on benzyl bromide,  $\text{CH}_2\text{PhBr} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{Ph} \cdot \text{OH} + \text{HBr}$ , equilibrium is reached when two-thirds of the benzoyl bromide has been changed. Here, too, the values of  $k = 1/t \cdot \log[(2-x)/(2-3x)]$  show gradual diminution.

These results are not all easily explainable, but it is evident that the introduction of a carboxyl group into the molecule of benzyl bromide renders the bromine atom less mobile, this action being most marked in the para-position and least in the meta-position.

T. H. P.

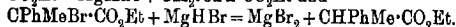
**Action of Magnesium on Ethyl Phenylbromoacetate.** J. S. ZALKIND and A. V. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 476—478).—The action of magnesium on ethyl phenylbromoacetate is

the presence of ether and a crystal of iodine and subsequent decomposition of the product with water yield ethyl  $\alpha$ -diphenylacetoacetate and ethyl phenylacetate, the reactions involved being expressed by the equations: (1)  $\text{CHPhBr}\cdot\text{CO}_2\text{Et} + \text{Mg} = \text{MgBr}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  and this  $+ \text{H}_2\text{O} = \text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et} + \text{MgBr}\cdot\text{OH}$ ; (2)  $2\text{MgBr}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et} = \text{MgBr}\cdot\text{CHPh}\cdot\text{C}(\text{OEt})(\text{O}\cdot\text{MgBr})\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  and this  $+ 2\text{H}_2\text{O} = \text{MgBr}\cdot\text{OH} + \text{Et}\cdot\text{OH} + \text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  (compare Zalkind, A., 1907, i, 22; Reformatski, A., 1907, i, 23; Zeltner, A., 1908, i, 243).

T. H. P.

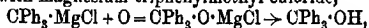
**Action of Magnesium on Esters of  $\alpha$ -Bromo- $\alpha$ -phenylpropionic and Diphenylbromoacetic Acids.** J. S. ZALKIND and Mlle. M. S. PESCHEROVA (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 478—488).—Zalkind and Baskov (preceding abstract) have shown that, like other  $\alpha$ -bromo-esters, ethyl phenylbromoacetate yields derivatives of ethyl acetoacetate when treated with magnesium and subsequently with water. In order to ascertain to what extent this reaction is general for  $\alpha$ -bromo-derivatives of phenyl-substituted acids, the authors have investigated the action of magnesium on ethyl  $\alpha$ -bromo- $\alpha$ -phenylpropionate and diphenylbromoacetate. These esters are highly unstable, the former readily losing a molecule of hydrogen bromide and the latter exchanging a bromine atom for a hydroxyl or ethoxyl group. This mobility of the bromine atom is also manifest in the interaction of the esters and magnesium, which dissolves easily in both of them in presence of dry ether, so that the addition of iodine is unnecessary for the initiation of the reaction.

The decomposition by means of water of the products formed proceeds quite otherwise than with the esters of  $\alpha$ -bromo-acids previously investigated. Thus, with the former of the two esters, the products consist principally of ethyl  $\alpha$ -phenylpropionate (up to 50%) and of 1–9% of ethyl atropate, the main reaction taking place thus:  $\text{CPhMeBr}\cdot\text{CO}_2\text{Et} + \text{Mg} = \text{MgBr}\cdot\text{CPhMe}\cdot\text{CO}_2\text{Et}$  and this  $+ \text{H}_2\text{O} = \text{MgBr}\cdot\text{OH} + \text{CHPhMe}\cdot\text{CO}_2\text{Et}$ . The mechanism of the formation of atropic ester is probably expressed by the equations:  $\text{MgBr}\cdot\text{CPhMe}\cdot\text{CO}_2\text{Et} = \text{MgHBr} + \text{CH}_2\cdot\text{CPh}\cdot\text{CO}_2\text{Et}$  and

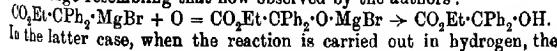


The expected diphenyldimethylacetoacetic ester is obtained in such small proportion that it could not be separated in the pure state.

No acetoacetate derivative at all is obtained from ethyl diphenylbromoacetate, which gives an organo-magnesium compound distinguished by its ready oxidisability. Although the reaction is carried out in a reflux apparatus, so that the vapour of the ether mixes with the air, decomposition of the product of the reaction by means of water gives benzoic acid in 50% yield. Use of an atmosphere of hydrogen causes the amount of benzoic acid to diminish but not to vanish. A similar tendency to oxidation was observed by Schmidlin (A., 1906, i, 392; 1907, i, 26) with magnesium triphenylmethyl chloride,



this change resembling that now observed by the authors:



In the latter case, when the reaction is carried out in hydrogen, the

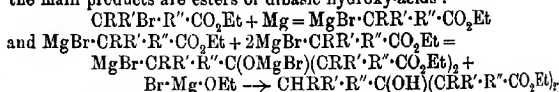
products consist of diphenylacetic acid (up to 55% yield), benzoic acid, ethoxydiphenylacetic acid and a very small proportion of a crystalline acid, m. p. 275°, the constitution of which was not determined; the ethoxy-acid seems to be formed during the preparation of the original ester from the bromo-anhydride of  $\alpha$ -bromodiphenylacetic acid and alcohol.

Thus, of these bromoacetic esters, the phenyl derivative yields 65% of ketonic ester and 22% of phenylacetic ester, the phenylmethyl derivative gives about 50% of ketonic ester and 9% of atropic ester, whilst the diphenyl derivative undergoes no condensation. This varying behaviour is regarded as related to the degree of saturation of the fundamental carbon atom and of the bromine atom; as the hydrogen atom of the first ester is displaced by methyl and then by phenyl, the carbon atom attached to the bromine atom becomes increasingly saturated and the bromine atom itself decreasingly so; from this result the diminishing tendency of the carbon to condensation and the increasing mobility of the bromine atom or the magnesium derivative.

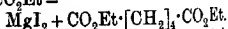
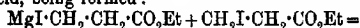
*Ethyl  $\alpha$ -bromo- $\alpha$ -phenylpropionate*,  $\text{CMePhBr}\cdot\text{CO}_2\text{Et}$ , prepared from the bromo-anhydride of  $\alpha$ -bromo- $\alpha$ -phenylpropionic acid and alcohol, was obtained as an oily, somewhat impure liquid,  $D_4^{20}$  1.3369.

*Ethoxydiphenylacetic acid*,  $\text{OEt}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , forms crystals, m. p. 114–115°, and has the normal molecular weight in boiling ether. [Is silver salt was analysed. T. H. P.]

**Action of Magnesium on Esters of  $\beta$ -Halogenated Acids.** J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 488–504).—The action of magnesium on esters of  $\alpha$ -halogenated acids yields principally ketonic esters, whereas with most carboxylic compounds the reaction goes further and leads to the formation of alcohols. The failure of the latter reaction with  $\alpha$ -bromo-esters may depend on the immediate proximity of the group  $\text{:C}\cdot\text{MgBr}$  to the unsaturated carboxyl group, so that the carbon and the magnesium of the group  $\text{:C}\cdot\text{MgBr}$  become more saturated and less reactive. Greater separation of the halogen from the carboxyl group should therefore be accompanied by increase in the capacity of the organo-magnesium compound to react, and this is actually found to be the case. With  $\beta$ -halogenated esters, indeed, the main products are esters of dibasic hydroxy-acids:



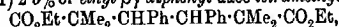
To a slight extent, however, the change proceeds in the direction of the Wurtz-Fittig reaction, esters of dibasic acids, for example, adipic acid, being formed:



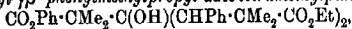
The dibasic hydroxy-acids forming the principal products are either viscous liquids or amorphous, colourless solids, which cannot be distilled unchanged even in a vacuum. In spite of the  $\beta$ -position of the hydroxyl to the two carboxyl groups, only the simplest of these acids, obtained from ethyl  $\beta$ -iodopropionate, is able to form a lactone.

*Ethyl β-bromo-β-phenylpropionate*,  $\text{CHPhBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , prepared by the action of hydrobromic acid on ethyl cinnamate, forms a viscous oil with a faint, pleasant odour,  $D_4^{20}$  1.3751,  $D_4^{25}$  1.3559,  $n_D^{20}$  1.54246. When treated with dry ether, magnesium and a crystal of iodine, it yields ethyl  $\beta\gamma$ -diphenyladipate (9.4%), ethyl  $\beta$ -phenylpropionate (35.5%), and ethyl  $\gamma$ -hydroxy- $\beta\delta$ -diphenyl- $\gamma\beta'$ -phenylethylpimelate (47.4%),  $\text{H}\cdot\text{C}(\text{CH}_2\cdot\text{CH}_2\text{Ph})(\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ . The acid,  $\text{C}_{27}\text{H}_{28}\text{O}_5$ , corresponding with this ester, forms an amorphous, white powder, m. p. 108–111°, and has the normal molecular weight in boiling acetone; its silver salt was analysed.

$\beta$ -Bromo- $\beta$ -phenyl- $\alpha\alpha$ -dimethylpropionic acid,  $\text{CHPhBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , prepared from phenoxypivalic acid and hydrobromic acid, forms prismatic crystals, m. p. 122°, and its ethyl ester,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{Br}$ , prepared from the chloro-anhydride and ethyl alcohol, is a colourless, viscous oil, with a pleasant but slightly irritating odour, b. p. (decomp.) 193–194°/44 mm., 163–164°/17 mm.,  $D_4^{20}$  1.3494,  $D_4^{25}$  1.3274,  $n_D^{20}$  1.54654. The ester reacts with difficulty with magnesium, giving a product which with water yields (1) 2.5% of ethyl  $\beta\gamma$ -diphenyl- $\alpha\alpha\alpha\alpha$ -tetramethyladipate,



which forms crystals, m. p. 145.5–146°, and has the normal molecular weight in freezing benzene; (2) 36% of ethyl phenylpivalate, b. p. 235–240° (decomp.), 136–138°/13 mm. and (3) 50% of ethyl  $\gamma$ -hydroxy- $\beta\delta$ -diphenyl- $\gamma\beta'$ -phenylmethylpropyl- $\alpha\alpha\alpha\alpha$ -tetramethylpimelate,



m. p. 60–70°; the corresponding acid,  $\text{C}_{23}\text{H}_{29}\text{O}_5$ , an amorphous, white powder, m. p. 74–80°, which has the normal molecular weight in boiling acetone, its silver salt,  $\text{C}_{23}\text{H}_{28}\text{O}_5\text{Ag}_2$ , and its diacetyl derivative,  $\text{C}_{25}\text{H}_{42}\text{O}_6$ , white, amorphous compound, were prepared.

Ethyl  $\beta$ -iodopropionate and magnesium readily react, giving a product which with water yields: (1) 13.5% of ethyl propionate; (2) 5.6% of ethyl adipate, and (3) 61% of ethyl  $\gamma$ -hydroxy- $\gamma$ -ethylpimelate, which on conversion to the corresponding acid,  $\text{C}_9\text{H}_{16}\text{O}_5$ , undergoes partial conversion into the lactonic acid,  $\text{C}_9\text{H}_{14}\text{O}_4$ .

T. H. P.

**Action of Magnesium on Ethyl  $\beta$ -Bromo- $\beta$ -phenylisobutyrate.** J. S. ZALKIND and S. N. GRABOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 504–507)—This reaction is similar to those obtained with other  $\beta$ -halogenated acids, the products being ethyl  $\alpha$ -benzylpropionate (31%) and ethyl  $\gamma$ -hydroxy- $\beta\delta$ -diphenyl- $\gamma\beta'$ -phenylisopropyl- $\alpha\alpha$ -dimethylpimelate (55%).

$\beta$ -Bromo- $\beta$ -phenyl- $\alpha$ -methylpropionic acid,  $\text{CHPhBr}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , prepared by heating  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionic acid in a sealed tube with hydrobromic acid, forms small crystals, m. p. 106–107°, with a faint odour which attacks the mucous membrane. The corresponding ethyl ester,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{Br}$ , is a pale yellow liquid with a faint, but irritating odour,  $D_4^{20}$  1.1361,  $D_4^{25}$  1.1342,  $n_D^{20}$  1.4958.

$\gamma$ -Hydroxy- $\beta\delta$ -diphenyl- $\gamma\beta'$ -phenylisopropyl- $\alpha\alpha$ -dimethylpimelic acid,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{C}(\text{OH})(\text{CHMe}\cdot\text{CH}_2\text{Ph})\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , is a white, amorphous compound, m. p. 104–105°, and has the normal molecular weight in boiling ether. Its silver salt,  $\text{C}_{29}\text{H}_{33}\text{O}_5\text{Ag}_2$ , and the silver salt of its acetyl derivative,  $\text{C}_{31}\text{H}_{35}\text{O}_6\text{Ag}_2$ , were prepared and analysed.

T. H. P.



**Transformation of  $\beta\gamma$ -Unsaturated Acids by Ultra-violet Light.** R. STOEHRER and H. STOCKMANN (*Ber.*, 1914, 47, 1793—1795).—As a representative of the  $\beta\gamma$ -ethylenic acids,  $\gamma$ -phenylvinylacetic acid, in benzene solution, has been exposed to ultra-violet light. Although the *allo*-form could not be obtained solid, the crystalline *allo*-amide was isolated and converted by separate illumination into the stable variety.

$\gamma$ -Phenylvinylacetic acid (Fichter, A., 1907, i, 87) is very sparingly soluble in light petroleum, so this solvent was used to extract the *allo*-variety, about 20% of this being formed in a week or two. The crude acid was treated with sodium ethoxide, the dry sodium salt converted into the acid chloride, and this poured into concentrated aqueous ammonia. The brown mass was recrystallised and yielded *allo*-phenylvinylacetamide,  $C_{10}H_{11}ON$ , in white needles, m. p. 85—86°. The stable amide, m. p. 130°, and anilide, m. p. 94.5—95°, were prepared from the corresponding chloride.

J. C. W.

**$\beta$ -2-Naphthoylpropionic Acid.** M. GIUA (*Ber.*, 1914, 47, 2115—2116).—Borsche and Sauernheimer have recently described the above acid as the sole product of the condensation of succinic anhydride and naphthalene by aluminium chloride (this vol., i, 839). The author had already shown that both the  $\alpha$ - and  $\beta$ -naphthalene derivatives are obtained in equal quantities when the reaction proceeds slowly in the cold (*Rend. Soc. Chim. Ital.*, 1912, 239). The methyl ester of the  $\alpha$ -acid is an oil, whilst methyl  $\beta$ -2-naphthoylpropionate forms colourless needles, m. p. 74°.

J. C. W.

**$\psi$ -Esters of *ortho* Dicarboxylic Acids.** ALFRED KIRPAL (*Monatsh.*, 1914, 35, 677—696).—By treating  $\alpha$ -ethyl hydrogen hemipinate with thionyl chloride in the cold, or, better, by heating it with thionyl chloride and an excess of carbon tetrachloride on the water-bath (in the absence of carbon tetrachloride, the latter method yields hemipinic anhydride),  $\alpha$ -ethyl hemipinate- $\psi$ -chloride,  $C_6H_5(OMe)_2 \begin{smallmatrix} \text{CCl(OEt)} \\ \text{CO} \end{smallmatrix} O$ ,

m. p. 102°, colourless prisms, is obtained (compare Egerer and Meyer, A., 1913, i, 269). The ester- $\psi$ -chloride is stable in boiling benzene, but is converted by not too prolonged treatment with cold absolute

alcohol into  $\psi$ -ethyl hemipinate,  $C_6H_5(OMe)_2 \begin{smallmatrix} C(OEt)_2 \\ CO \end{smallmatrix} O$ , m. p. 64°,

colourless prisms or plates. The  $\psi$ -ester changes to the normal ester (m. p. 72°) at its b. p., and is rapidly converted into  $\alpha$ -ethyl hydrogen hemipinate by alcoholic hydrogen chloride; one ethyl group is removed as ethyl iodide even by cold aqueous hydriodic acid (compare Egerer and Meyer, *loc. cit.*). The  $\psi$ -ester is changed to the normal ester by alcoholic sodium ethoxide, slowly at room temperature, almost instantly by heating. That this change is due, not to intramolecular rearrangement, but to the addition of ethyl alcohol and its subsequent elimination in a different manner, is proved by the fact that the  $\psi$ -ethyl ester and methyl-alcoholic sodium methoxide yield exclusively

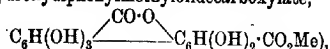
$\beta$ -methyl  $\alpha$ -ethyl hemipinate,  $OMe \cdot C : C(OMe) \cdot \begin{smallmatrix} C-CO_2Et \\ | \\ CH:CH-C-CO_2Me \end{smallmatrix}$ , m. p. 88°, glis-

tening needles. This ester has also been obtained from  $\alpha$ -ethyl silver hemipinate and methyl iodide, and by the action of alcoholic sodium methoxide on normal ethyl hemipinate (again an example of the addition and subsequent elimination of an alcohol).

$\beta$ -Ethyl hydrogen hemipinate and thionyl chloride yield hemipinic anhydride by warming. At room temperature the product is (impure)  $\beta$ -ethyl hemipinate chloride,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{COCl}$ , which behaves like a normal acid chloride, yielding chiefly the normal diethyl ester by treatment with cold alcohol, and  $\beta$ -ethyl hydrogen hemipinate by treatment with water. The  $\beta$ -ester chloride changes to the  $\alpha$ -ester- $\psi$ -chloride, slowly at the ordinary temperature, more rapidly by heating in an indifferent solvent.

Some experiments are recorded on the estimation by Ziesel's method of mobile methoxy- and ethoxy-groups. C. S.

**Gallic Acid.** ERW. SCHWENK (*J. pr. Chem.*, 1914, [ii], 90, 53—60).—An account of unsuccessful attempts to prepare 2:3:4:2':3':4'-hexahydroxydiphenyl-6:6'-dicarboxylic acid, of which ellagic acid is considered to be the anhydride, by oxidising gallic acid and its methyl ester with ferric chloride. Oxidation of methyl gallate in glacial acetic acid solution results in the formation of ellagic acid. The latter acid is also formed when the oxidation is carried out in boiling aqueous solution, but in this case is accompanied by a substance (probably methyl pentahydroxydiphenylmethylolidecarboxylate,



from which it could not be separated.

Ellagic acid is not produced when gallic acid itself is oxidised with ferric chloride.

*Methyl 3:4:5-triacetoxybenzoate*, prepared by heating methyl gallate with acetic anhydride, forms rhomboidal crystals, m. p. 120—122°.

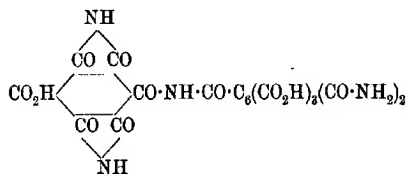
*Ethyl 3:4:5-triacetoxybenzoate* crystallises in rhombs, m. p. 123—125°.

Methyl dibromogallate sinters at 155°, m. p. 160—161° (compare Biétrix, A., 1893, i, 343), and on acetylation yields *methyl 2:6-dibromo-3:4:5-triacetoxybenzoate*, which crystallises in white rhombs, m. p. 150—152°. F. B.

**Mellitic Acid.** HANS MEYER and KARL STEINER (*Monatsh.*, 1914, 35, 475—518).—After a review of the history of mellitic acid, the author gives details for the preparation of this substance by oxidising pine-wood charcoal with nitric acid, the yield of crude product being 48% of the charcoal taken (compare Meyer, this vol., ii, 267).

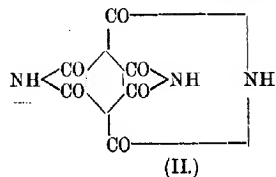
The ammonium salt forms crystals (with  $9\text{H}_2\text{O}$ ) which belong to the rhombic system ( $a:b:c=1.5443:1.05545$ ; compare Wyrubov, *Bull. Soc. chim.*, 1894, [iii], 11, 121). A closer examination of the thermal decomposition of this salt has been made; chemical change commences at 100° and is complete at 200°; above this temperature further decomposition ensues with formation of derivatives of pyromellitic acid. The product at 200° is a yellowish-white powder and can be separated by water, as described by Wöhler, into insoluble

paramide and soluble ammonium euchronate (*Annalen*, 1841, 37, 268). Analysis of the euchronic acid indicates a formula  $C_{12}H_{11}O_8N_3$ , instead of the earlier  $C_{12}H_9O_8N_3$ ; the acid is tetrabasic, and as diazomethane introduces seven methyl groups, there must also be present three  $\cdot CO \cdot NH \cdot CO \cdot$  groups; on hydrolysis, euchronic acid is converted completely into mellitic acid, whilst when strongly heated it gives pyromellitic acid with partial decomposition. From these results the

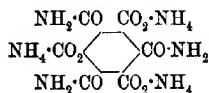


prepared, but on crystallisation from quinoline is obtained in yellow needles.

When amorphous paramide,  $C_{12}H_9O_8N_3$ , is treated with concentrated ammonia solution, a pentamide,  $C_{12}H_9O_8N_5$ , of mellitic acid is obtained; the addition of only two molecules of ammonia leads the authors to suggest that instead of possessing the structure (formula I), paramide has two of its carbonyl groups linked differently from the remainder, namely, between the para-positions (as, for example, in formula II).



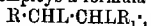
by decomposition with the formation of a deep blue substance. If the mellitic anhydride is in suspension in ether or benzene, dry ammonia converts it into an ammonium salt (annexed formula), a colourless, crystalline powder soluble in water.



The formation and properties of trimethylparamide (compare Meyer and Steiner, A., 1913, i, 204) and of the anhydrides of mellitic acid (A., 1913, i, 368) are discussed. On boiling with methyl alcohol the dianhydride,  $C_{12}H_2O_{10}$ , was converted into a mixture of esters in which a dimethyl ester predominated, whilst the trianhydride,  $C_{12}O_9$ , also gave a mixture of which the only isolable constituent was a tetramethyl ester, crystals, m. p. 70—110°.

D. F. T.

The Preparation of *l*- and *d*-Cinnamic Acid by Asymmetric Induction. EMIL ERLKENMEYER [with G. HILGENDORFF and F. LANDSBERGER] (*Biochem. Zeitsch.*, 1914, 64, 296—365).—It is shown that optical activity can be "induced" in cinnamic acid when the latter is heated to 163° with optically active tartaric acids. When *d*-tartaric acid is used, a small amount of *l*-cinnamic acid is obtained (which can be dissolved out of the fusion with light petroleum) together with a mixture of the mono- and di-cinnamyl tartrates. The latter on treatment with cold sodium carbonate solution are hydrolysed, and a cinnamic acid preparation can be obtained therefrom, of which  $[\alpha]_D$  reaches  $-20^\circ$ . It is assumed that the cinnamic acid exists in optically active forms before it forms the esters. The cinnamates can also be hydrolysed by heating with water. The optically active preparations of cinnamic acid obtained in this way are free from tartaric acid, as, on heating, they sublime without the smallest trace of charring, and are completely soluble in light petroleum. The cinnamic acid preparations lose their optical activity on sublimation, or on treatment of their solutions with a few drops of sodium hydroxide solution. The dicinnamate can be more advantageously prepared by heating the *d*- or *l*-tartaric acid with cinnamic anhydride. In addition to the ester, cinnamic acid is formed in the reaction and this is optically active, the direction of the rotation depending on the rotation of the tartaric acid used, the *l*-form being obtained from the *d*-tartaric acid, and the *d*-form from *l*-tartaric acid. The cinnamyl tartrate in both cases also yields an optically active acid on hydrolysis. On addition of bromine to the *l*-acid, an optically inactive bromine additive product was obtained. The author develops at length his conceptions of relative asymmetry (compare A., 1911, i, 780), and shows that cases of stereoisomerism in substances containing no asymmetric carbon atom are conceivable when his models are employed. To represent the asymmetry of unsaturated compounds, such as cinnamic acid, he employs a formula of the type



of which twelve "relative" isomerides are possible. In this formula *L* represents an unoccupied space. The author also recapitulates his various experiments on induced asymmetry.

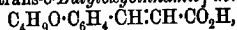
S. B. S.

Rearrangements of Higher Alkylcoumaric [*o*-Alkyloxy-cinnamic] Acids by Ultra-violet Light. R. SROERMER and H. LADEWIG (*Ber.*, 1914, 47, 1795—1803).—In some previous experiments (compare A., 1911, i, 295) it was found that when the hydroxyl-hydrogen atom of coumaric acid is displaced by the methyl or ethyl group, the readiness with which the acid is transformed into the coumarinic acid increases, but falls again with the introduction of the propyl group. It is now found that this characteristic is still further diminished in the case of the butyl radicles, only to rise again with the *iso*amyl group.

An interesting feature about these acids is that many of their salts are soluble in benzene and ether; for example, calcium amyloxy-cinnamate may even be extracted by ether. The heats of combustion and dissociation constants of the acids were recorded in A., 1913, ii, 297. The *iso*amyl isomerides are exceptionally similar in m. p.'s and solu-

bilities in organic media. Owing to their similarity, it was of course impossible to separate the isomerides as such, but their amides differ sufficiently in solubility to be of service. These compounds could only be hydrolysed by Bouveault's method, whereby the labile form was at the same time converted into the stable.

*n*-Butylcoumaric [trans-*o*-Butyloxycinnamic] acid,



was prepared by heating the sodium salt of methyl coumarate with *n*-butyl iodide, followed by hydrolysis of the ester. The pure acid, as obtained from the calcium salt, crystallises from light petroleum (solubility at 17°, 0.447%) in rhombic leaflets, m. p. 89–90°, and exhibits no fluorescence in alkaline solution, which it might do if not free from coumaric acid. The amide forms silky, white needles, m. p. 143–144°, and is almost insoluble in light petroleum. *n*-Butylcoumarinic [cis-*o*-Butyloxycinnamic] acid is obtained to the extent of about 70%, when the isomeride is illuminated for ten days or so, or it may be prepared directly from coumarin. It is more soluble than the *trans*-acid (16.4% in light petroleum) and crystallises in small, thick tablets, m. p. 53–54°. Similarly, when the *trans*-amide is exposed to the light for fourteen days in methyl alcohol, 95% is transformed into the *cis*-amide,  $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$ , which forms white, matted needles, m. p. 91°. *trans*-*o*-isoButyloxycinnamic acid forms white crystals, m. p. 98°, solubility in light petroleum, 0.385% at 18°, and the amide separates in white needles, m. p. 140°. The *cis*-acid is formed to the extent of about 67% by ten days' illumination, has m. p. 75°, and dissolves in light petroleum to the extent of 4.61% at 18°. The *cis*-amide, m. p. 105°, is formed in 95–99% yield by exposing the isomeride to light.

*trans*-*o*-isoAmyloxycinnamic acid,  $\text{C}_{14}\text{H}_{18}\text{O}_2$ , was also purified by conversion into the calcium salt. It forms very characteristic rhombic crystals, m. p. 79–80°, from light petroleum (solubility 1.56% at 18°), and the amide crystallises in slender, white needles, m. p. 144–145°. The *cis*-acid, prepared directly from coumarin, crystallises from light petroleum (solubility, 1.53%) in sheaves of slender, white needles, m. p. 80–80.5°. The m. p. of a mixture of the acids was depressed nearly 20°. The *cis*-amide forms slender, white needles, m. p. 76–77°. It was prepared directly from the *trans*-acid, by illuminating the isomeride for ten days in methyl alcohol (yield 90%), and also from the mixture obtained by exposing *trans*-amyloxycinnamic acid to the light for twenty days (80% of the calculated yield). The sodium, copper, barium, and calcium salts of the isomeric acids are described. J. C. W.

Esterifications by Ultra-violet Light. R. STOERMER and H. LADEWIG (*Ber.*, 1914, 47, 1803–1806).—It has been accidentally discovered that, when alcoholic solutions of *trans*-cyclohexane-1:4-dicarboxylic acid and *trans*-cyclopentane-1:2-dicarboxylic acid are exposed to ultra-violet light, they are partly converted into mono- and di-esters and not transformed into the *cis*-modifications, as was expected. Benzoic acid is also esterified under these conditions (30% in 8 days) and the reaction is still further promoted by the presence of a trace of hydrochloric acid (56% in 8 days). Cinnamic acid is scarcely

affected without the addition of a trace of hydrochloric acid, but the yield of ester may then reach 37% in 8 days.

By illuminating *trans*-cyclohexane-1:4-dicarboxylic acid (Baeyer, A., 1888, 1074) in methyl alcohol for ten days, a 10% yield of the *methyl hydrogen* salt,  $C_6H_{14}O_4$ , was obtained, in small, white needles, m. p.  $125^\circ$ , whilst, after longer exposure, high yields of the dimethyl ester, m. p.  $71^\circ$ , resulted, sometimes mixed with the hemi-ester. Similarly, ten days' illumination of *trans*-cyclopentane-1:2-dicarboxylic acid (Perkin, T., 1894, 65, 572) gave rise to the *methyl hydrogen* salt,  $C_5H_{12}O_4$ , white needles, m. p.  $45^\circ$ , whilst thirty days' exposure to the light resulted in the formation of both esters, in 10% yields.

J. C. W.

**Preparation of Acetoacetanilide-*p*-carboxylic Acid.** FARBEN-FABRIKEN VORM. FRIDR. BAYER & CO. (D.R.-P. 272530).—When ethyl acetoacetanilide-*p*-carboxylate, obtained by heating ethyl *p*-aminobenzoate with ethyl acetoacetate in absence or presence of a suitable diluent, is treated with an alkali hydroxide and subsequently with hydrochloric acid, it is converted into acetoacetanilide-*p*-carboxylic acid.

T. H. P.

**The Preparation of a Lævorotatory Benzaldehyde by Asymmetric Induction by means of *d*-Tartaric Acid; Conversion of the same into *l*-Mandelonitrile and *d*-Mandelic Acid; the Nature of Enzymatic Reactions.** EMIL ERLKENMEYER [with F. LANDSBERGER and G. HILGENDORFF] (*Biochem. Zeitsch.*, 1914, 64, 382—392).—If a carbonyl derivative is regarded as unsaturated, then, if the author's method is adopted, it can be represented by the formula  $C_6H_5 \cdot CHL \cdot OL$ , where L indicates an unoccupied position. Such a substance should contain an asymmetric carbon atom and be resolvable into optical isomerides. By "induction" by means of *d*-tartaric acid, a *l*-form can be obtained if the acid and aldehyde are heated together in alcoholic solution. The *l*-aldehyde yields with hydrocyanic acid a *l*-nitrile, from which by hydrolysis a *d*-acid is obtained. It is suggested that asymmetric synthesis of the nitrile by means of emulsin is a case of "induction," and that it is by this method that enzymes can act.

S. B. S.

**Reaction of Nitroprussides with Some Ketones. II.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 812—820. Compare A., 1913, i, 606).—When a solution of nitroprusside in methyl alcohol containing acetophenone is added at  $0^\circ$  to a solution of sodium methoxide or ethoxide, the salt,  $\left[ \begin{smallmatrix} Fe(CN)_5 \\ C_8H_7O_2N \end{smallmatrix} \right] Na_4 \cdot H_2O$ , is precipitated. It is a bright red powder, giving precipitates with solutions of iron and copper salts. The violet *copper* salt,  $\left[ \begin{smallmatrix} Fe(CN)_5 \\ C_8H_7O_2N \end{smallmatrix} \right] Cu_2$ , was prepared. The violet aqueous solution of the sodium salt becomes deep yellow on keeping, and ferroaquopentacyanide and the sodium salt of oximinoacetophenone can be isolated from it. The acid *sodium*

salt,  $\left[\text{Fe}(\text{CN})_5\right] \text{Na}_3$ , obtained by the action of acid on the sodium salt already mentioned, is a violet powder which yields blue solutions.

Similar compounds can be prepared from other ketones. Bromoacetophenone yields the salt,  $\left[\text{Fe}(\text{CN})_5\right] \text{Na}_3 \cdot \text{MeOH}$ . Acetylacetone gives the salt,  $\left[\text{Fe}(\text{CN})_5\right] \text{Na}_4$ .

R. V. S.

**Dimethylallylacetophenone and its Oxidation Products.** J. MEYERINGH and A. HALLER (*Compt. rend.*, 1914, 158, 1957—1961, Compare Haller and Bauer, this vol., i, 549).—*aa*-Dimethyl- $\alpha$ -allylacetophenone on oxidation in the cold with 3% potassium permanganate containing 1% of potassium hydroxide yields  $\beta$ -benzoyl- $\beta$ -methylpentane- $\delta$ -diol, obtained by Ramart-Lucas and Haller from  $\delta$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane on boiling with water (compare this vol., i, 695). Attempts to prepare a benzoyl derivative or a phenylurethane from the diol by the ordinary methods only yielded the dimeride of  $\delta$ -oxido- $\beta$ -benzoyl- $\beta$ -methylpentane (*loc. cit.*). A benzoyl derivative,  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OBz}$  or  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CH}(\text{OBz})\cdot\text{CH}_2\cdot\text{OH}$ , m. p. 129°, was, however, obtained by the action of benzoyl chloride in the cold in the presence of pyridine. In the original oxidation, the amount of potassium permanganate used was equivalent to two atoms of oxygen. If the amount is increased to be equivalent to three atoms of oxygen the product is  $\gamma$ -benzoyl- $\alpha$ -hydroxy- $\gamma$ -methylvaleric acid,  $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 152°, which on neutralising with ammonia yields with silver nitrate a silver salt, a white powder, blackening in light. Oxidation of the original acetophenone in warm solution yields a certain amount of the above diol, together with benzoic acid and carbon dioxide.

W. G.

**Syntheses by means of Sodamide. The Alkylcyclopentanones, Obtained by Hydrogenation of Unsaturated Derivatives Followed or not by Alkylation.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1914, 158, 1739—1743).—2:4-Dibenzylidene-1-methylcyclopentan-3-one on reduction in alcoholic solution with reduced nickel in an atmosphere of hydrogen (compare Brochet, this vol., i, 645) readily yields 2:4-dibenzyl-1-methylcyclopentan-3-one, a viscous liquid, b. p. 232—233°/17 mm., which in ethereal solution on treatment with sodamide, followed by methyl iodide, furnishes 1:3-dibenzyl-1:3:4-trimethylcyclopentan-2-one, m. p. 74°, b. p. 228°/17 mm. The latter ketone on boiling in xylene solution with sodamide yields a compound, m. p. 138—139° (corr.), which is either  $\alpha\delta$ -dibenzyl- $\alpha\beta$ -dimethyl or  $\alpha\delta$ -dibenzyl- $\alpha\gamma$ -dimethylhexoamide.

1:4-Dimethyl-1:3:3-triallylcyclopentan-2-one also undergoes hydrogenation by the above process, giving 1:4-dimethyl-1:3:3-tripropylcyclopentan-2-one, a colourless, viscous liquid, b. p. 145°/15 mm. (corr.),  $D_4^{20}$  0.8955,  $n_D^{20}$  1.4649,  $[\alpha]_D^{20} + 7.10'$ , which on boiling with sodamide in xylene gives an amide, b. p. 200—205°/17 mm.,  $[\alpha]_D^{18} + 18.32'$ , which is either  $\beta\gamma$ -dimethyl- $\alpha\alpha$ -dipropyl- or  $\alpha\gamma$ -dimethyl- $\alpha\delta$ -dipropyl-octoamide.

The following conclusions are drawn from the series of researches: (1) cyclopentanone itself does not readily undergo alkylation, but gives condensation products in the presence of sodamide and an alkyl

iodide. (2) This is almost as true of 1-methylcyclopentan-3-one, although moderate yields of 2-derivatives are obtained. The best yields are obtained by using 2-alkyl or 2:5-dialkyl derivatives of cyclopentanone. (3) All the 1:1:4:4-tetra-alkylcyclopentanones, on boiling with sodamide in benzene or toluene yield amides of substituted aliphatic acids. (4) Starting with an active cyclopentanone the successive introduction of 1, 2, 3, or 4 alkyl groups into the positions 1 and 4, with respect to the :CO group, produces a diminution in the specific rotatory power of the substances.

W. G.

The Allylcyclohexanones and the Methylallylcyclohexanones. R. CORNUBERT (*Compt. rend.*, 1914, 158, 1900—1903).—The author has prepared all the allyl derivatives of the type  $\cdot\text{CR}_2\cdot\text{CO}\cdot\text{CR}_2$  theoretically possible from cyclohexanone, 1-methylcyclohexan-2-one, 1-methylcyclohexan-3-one and 1-methylcyclohexan-4-one by Haller's method (*A.*, 1913, i, 629).

1-Allylcyclohexan-2-one,  $\text{CH}_2 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_{11}) \end{array} \right\rangle \text{CO}$ , is a colourless, mobile liquid, b. p.  $94^\circ/16$  mm. (corr.), giving an oxime, needles, m. p.  $71^\circ$ ; 1:3-diallylcyclohexan-2-one, a colourless, mobile liquid, b. p.  $118\text{--}120^\circ/15$  mm. (corr.), giving an oxime, prisms, m. p.  $77^\circ$ ; 1:1:3-triallylcyclohexan-2-one, a colourless, mobile liquid, with an unpleasant odour, b. p.  $147\text{--}148^\circ/15$  mm. (corr.), does not give an oxime; 1:1:3:3-tetra-allylcyclohexan-2-one, a colourless, slightly viscous liquid having a disagreeable odour, b. p.  $169\text{--}170^\circ/14$  mm. (corr.), does not give an oxime.

1-Methyl-3-allylcyclohexan-2-one, a colourless, mobile liquid, b. p.  $96\text{--}97^\circ/14$  mm. (corr.), giving an oxime, microscopic crystals, m. p.  $49^\circ$ ; 1-methyl-1:3-diallylcyclohexan-2-one, a colourless, mobile liquid, b. p.  $125\text{--}126^\circ/15$  mm. (corr.), does not give an oxime; 1-methyl-1:3:3-triallylcyclohexan-2-one, a colourless, slightly viscous liquid, b. p.  $150^\circ/15$  mm. (corr.), does not give an oxime.

1-Methyl-4-allylcyclohexan-3-one, a colourless, mobile liquid, b. p.  $100\text{--}103^\circ/17$  mm. (corr.), gives an oxime, slender needles, m. p.  $80\text{--}86^\circ$ ; 1-methyl-2:4-diallylcyclohexan-3-one, a colourless, mobile liquid, b. p.  $129\text{--}130^\circ/17$  mm. (corr.), gives an oxime, prisms, m. p.  $65^\circ$ ; 1-methyl-2:4:4-triallylcyclohexan-3-one, a colourless, slightly viscous liquid, b. p.  $154\text{--}155^\circ/16$  mm. (corr.), does not give an oxime; 1-methyl-2:2:4:4-tetra-allylcyclohexanone, a colourless, viscous liquid, with a disagreeable odour, b. p.  $179^\circ/16$  mm. (corr.), does not give an oxime.

1-Methyl-3-allylcyclohexan-4-one, a colourless, mobile liquid, b. p.  $105\text{--}106^\circ/16$  mm. (corr.), gives an oxime, needles, m. p.  $97\text{--}98^\circ$ ; 1-methyl-3:5-diallylcyclohexan-4-one, a colourless, mobile liquid, b. p.  $131\text{--}133^\circ/17$  mm. (corr.), gives an oxime, plates, m. p.  $73^\circ$ ; 1-methyl-3:5:5-triallylcyclohexan-4-one, a colourless, slightly viscous liquid, having a somewhat unpleasant odour, b. p.  $154\text{--}155^\circ/15$  mm. (corr.), does not give an oxime; 1-methyl-3:3:5:5-tetra-allylcyclohexan-4-one, a colourless, viscous liquid, with a somewhat unpleasant odour, b. p.  $169^\circ/14$  mm. (corr.), does not give an oxime.

The allylation in all cases gives two products separable by fractional distillation, the process being less easy as the allylation proceeds. All the monoallyl derivatives have an odour of menthone and



the yield of them is better the nearer the methyl group is to the ketone group, whilst the products of condensation are greater the more remote the methyl group is. In no case was an oxime obtainable when three or more alkyl groups were present attached to the carbon atoms adjacent to the carbonyl group. W. G.

The Present State of the Chemistry of Anthraquinone.  
ROBERT E. SCHMIDT (*Bull. Soc. chim.*, 1914, [iv], 15, i—xl).—A lecture delivered before the French Chemical Society. W. G.

Yields of Purpurogallin from the Oxidation of Pyrogallol with Peroxydase and Hydrogen Peroxide. A. BACH (*Ber.*, 1914, 47, 2125—2126).—The yields of purpurogallin obtained by Bach and Chodat (*A.*, 1904, i, 792) from pyrogallol by oxidation with peroxydase and hydrogen peroxide accord fairly well with the maximum yields obtained by Nierenstein and Spiers (*A.*, 1913, i, 1367), namely, approximately 16%. It has been stated, however, by de Stocklin (*Diss.*, Geneva, 1907) that yields as high as 50% can be obtained, and that the poorer yields of the former investigators were due to too high a concentration of hydrogen peroxide and too impure a specimen of peroxydase. That this explanation cannot be entirely correct is shown by the formation of a maximum yield of only 26% when the especially pure peroxydase obtained by ultra-filtration (Bach, this vol, ii, 691) is used, for this peroxydase was twenty times as active as that of de Stocklin; also variation of the concentration of the hydrogen peroxide did not affect the yield to any extent.

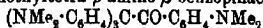
When a solution of purpurogallin in alcohol or acetone is diluted with three volumes of water and treated with peroxydase and hydrogen peroxide, there results a violet coloration which is slowly replaced by a brown. This reaction will detect two parts of purpurogallin in  $10^{-6}$  parts of solvent.

The most important factor for the formation of a good yield of purpurogallin in the oxidation of pyrogallol is probably, therefore, the rapid separation of the purpurogallin in the solid state. D. F. T.

Dimethylaminodihydroxybenzophenone. MAX WENZING (*Ber.*, 1914, 47, 2152—2156).—When an intimate mixture of tetramethyldiaminobenzophenone, resorcinol, and zinc chloride is heated, a violet colour is first produced, and on reaching 220° dimethylaniline is set free. The product at the first stage of the reaction dissolves in dilute hydrochloric acid with a reddish-violet colour, and is believed to be an additive compound of the structure  $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4)_2 \cdot \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , whilst the final product, produced from this by scission of dimethylaniline, is dimethylaminodihydroxybenzophenone,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , yellow needles or leaflets; hydrochloride, colourless prisms, decomp. at 230°; sulphate and oxalate, needles; zincchloride, pale yellow leaflets (with  $2\text{H}_2\text{O}$ ), decomp. at 225°.

The m. p. of the free base was not sharp, crystallisation from dilute solution giving needles, m. p. 165—167°, whilst it was possible to obtain leaflets, m. p. 171—172°, from more concentrated solution. It is suggested that the base may, like benzophenone, be capable of existence in two modifications of different m. p. D. F. T.

Octamethyltetra-amino- $\beta$ -benzopinacolin and its Reversed Pinacolin Rearrangement. S. FISCHL (*Monatsh.*, 1914, 35, 519—531).—Octamethyltetra- $p$ -amino- $\beta$ -benzopinacolin,



(Fischl, A., 1913, i, 466), is readily formed on heating, with the addition of a small quantity of dilute acid, a benzene solution of the pinacone of tetramethyldiaminobenzophenone. The pinacolin (*platinichloride*, microscopic, orange-yellow, rhombic tablets) when heated with an amyl-alcoholic solution of potassium hydroxide undergoes fission into hexamethyltri- $p$ -aminotriphenylmethane and  $p$ -dimethylaminobenzoic acid, thus demonstrating that the nuclear positions of attachment are the same in the pinacone as in the pinacolin.

Reduction of the pinacone with tin and hydrochloric acid or of the pinacolin with amalgamated zinc and hydrochloric acid (in which case a so-called reversed pinacolin rearrangement occurs; compare Biltz and Seydell, A., 1913, i, 297) gives rise to octamethyltetra-aminotetraphenylethylene (*platinichloride*, microscopic, orange-yellow, hexagonal prisms or needles; *stannochloride*, needles), which has already been obtained directly from tetramethyldiaminobenzophenone (Willstätter and Goldmann, A., 1906, i, 980). Sodium and boiling isoamyl alcohol reduce octamethyltetra-aminotetraphenylethylene to *s*-octamethyltetra-aminotetraphenylethane,  $\text{C}_6\text{H}_5(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_4$ , colourless, lustrous needles, which decompose above  $300^\circ$ ; *platinichloride*, microscopic, orange-yellow prisms. The substance, m. p.  $90^\circ$ , obtained by Schöpp by condensation of dimethylaniline with *s*-tetrabromoethane, and described as octamethyltetra-aminotetraphenylethane (A., 1881, 160), is shown to be in reality tetramethyldiaminodiphenylmethane.

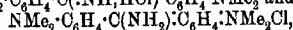
D. F. T.

The Preparation and Properties of the Compounds Given in the Tables of the Third Paper of Kehrman, Havas, and Grandmougin [Quinoneimide Dyes]. F. KEHRMAN (*Ber.*, 1914, 47, 2156—2159. Compare Kehrman, Havas, and Grandmougin, this vol., i, 868).—Details are given as to the preparation of the 1-aminophenazthionium, 3-aminophenazthionium, phenazoxonium, dimethylphenazoxonium, and 3-aminophenazoxonium salts mentioned in the earlier communication (*loc. cit.*).

[With Isaac FRANCEZ.]—The action of warm hydrochloric acid on 3-aminophenazthionium causes a reduction (Pummerer and Gassner, A., 1913, i, 991; this vol., i, 735), and the resulting chloroaminothiodiphenylamine separates as the hydrochloride, which can be oxidised to the corresponding dye by ferric chloride.

D. F. T.

The Constitution of Auramine. E. GRANDMOUGIN and S. FAYRE-AMBRUNYAN (*Ber.*, 1914, 47, 2127—2132).—In order to decide between the formulæ  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2 \cdot \text{HCl}) \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , and



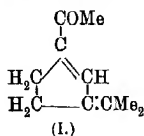
suggested by Graebe and Stock respectively for auramine, the purely chemical evidence being insufficient (compare Semper, A., 1911, i,

577; Strauss and Zeime, A., 1913, i, 992; Strauss and Bormann, A., 1910, i, 281), the authors have submitted the substance to a spectroscopic test; the result is in favour of the former constitution.

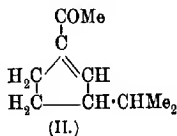
Alcoholic solutions of benzophenone, 4:4'-diaminobenzophenone, Michler's ketone, auramine base, auramine acetate and acetylauramine as well as a solution of auramine in concentrated sulphuric acid were examined; certain other derivatives have already been investigated (Grandmougin and Lang, A., 1909, i, 974). Unlike benzophenone, diaminobenzophenone possesses a complete absorption band with its head at  $340\mu$ . In Michler's ketone the band is situated at  $370\mu$ , whilst in auramine base, for which the curve is of the same type, the band is at  $300\mu$ . The absorption spectrum for auramine acetate has maxima at 310, 375 and  $435\mu$ , of which the two latter are the more marked, the deepening in the colour being indicative of salt formation at the chromophoric imino-group. With auramine dissolved in concentrated hydrochloric acid or 50% sulphuric acid, the solution is colourless with a maximum near  $265\mu$ , the dimethylamino-group also having now entered into salt-formation. The spectrum of acetylauramine resembles that of the other members of this group, but has a maximum at  $350\mu$ ; salt formation with this substance occurs at the dimethylamino-group with simultaneous rearrangement to the quinonoid configuration, so that in solution in acids, the spectrum is quite different from those of the preceding substances.

D. F. T.

New Investigations in the Camphor Group. IV. E. RIMINI (*Chem. Zentr.*, 1914, i, 1653—1654; from *Rend. della Soc. Chim. Ital.*, 1914, 27—28).—Traces of a substance of the probable formula  $C_{10}H_{15}Br_2$  are frequently formed during the preparation of bromopernitrosocamphor. *iso*Camphor is converted by reduction with



and



colloidal palladium into *dihydroisocamphor*. On oxidation, it yields acetone, succinic acid, and  $\alpha$ -ketoglutaric acid. The author is led to

propose the annexed formula (I) for *isocamphenone* and hence formula (II) for *isocamphor*. The latter has previously been considered as probable by Wallach.

H. W.

The Electrolytic Reduction of Carvoxime. H. RUPF and K. LÖFFL (*Ber.*, 1914, 47, 2150—2152).—The reduction of carvone and carvoxime by means of hydrogen and a catalyst has already been effected, the results varying somewhat with different conditions (compare Wallach, A., 1911, i, 469; this vol., i, 420; Vavon, A., 1911, i, 730; see also Law, T., 1912, 101, 1061). By reducing carvoxime at a lead cathode in aqueous-alcoholic solution containing sodium hydroxide at  $15^\circ$ , the authors have converted carvoxime into dihydrocarvone, no other reduction product being detected.

D. F. T.

**Thujone and Thujamenthone; Direct Passage from One to the Other.** MARCEL GODCHOT (*Compt. rend.*, 1914, 158, 1807—1808).—Thujone is readily converted into thujamenthone with an excellent yield by the action of hydrogen in the presence of reduced nickel at 175—180°.

W. G.

**Camphenecamphoric Acid and Hydroxycamphenilanic Acid.** S. V. HINTIKKA (*Chem. Zentr.*, 1914, i, 1573; from *Ann. Acad. Sci. Fennicae*, 1914, A, 5, iii, 1—8. Compare this vol., i, 409).—Hydroxycamphenilanic acid, m. p. 182—183°, is prepared in the following manner in a yield of about 15%. Camphene is dissolved in acetone and so much water added that the solution just remains clear. It is then oxidised by the gradual addition of solid potassium permanganate. Acetone, unchanged camphene, and camphenilone are removed in a current of steam. The filtered and concentrated solution is extracted with ether and treated with dry sodium carbonate. The acid is liberated from sparingly soluble sodium salt by means of sulphuric acid.

H. W.

**Constituents of Essential Oils: Effect of High Temperatures on Sesquiterpenes; Elimination of Terpinene; Artificial Production of the Blue Compound which is Present in Many Essential Oils.** F. W. SEMMLER and W. JAKUBOWICZ (*Ber.*, 1914, 47, 2252—2259).—Direct evidence in support of the view that terpenes and sesquiterpenes are nearly related has, hitherto, been lacking, for attempts to obtain the former by the decomposition of the latter have failed. It is now shown, however, that at about 330°, and under pressure, some typical sesquiterpenes break down into terpenes and, apparently, isoprene. Of course, these may react among themselves, and, consequently, it is not to be wondered at that isoprene could not be isolated as such. That it is indeed formed is shown by the secondary production of diterpenes. An important conclusion to be drawn is that the heat condensation of simple hydrocarbons, like isoprene and terpinene, has an optimum temperature above which degradation of the complex molecules takes place.

In the case of  $\alpha$ -gurjunene, the blue compound, which is frequently met with in essential oils, was produced.

Ten grams of pure  $\beta$ -gurjunene (this vol., i, 704) were heated in a sealed tube for twelve hours at 330°, when the brown, fluorescent oil was fractionated. The first fraction was boiled with sodium, and then had b. p. 60—65°/10 mm.,  $D_{20}$  0.8520,  $n_D$  1.4800, which agrees with  $\alpha$ -terpinene. This was confirmed by the formation of the nitrosite, m. p. 154°. The second fraction had b. p. 90—130°/10 mm., and was chiefly unchanged  $\beta$ -gurjunene. The final distillate had b. p. 170°/10 mm.,  $D_{20}$  0.9603,  $n_D$  1.54043, and therefore contained a diterpene, probably formed by the condensation of isoprene with  $\beta$ -gurjunene.

$\alpha$ -Gurjunene, with  $n_D$  1.15°, was submitted to the same treatment. The product had a dark blue colour. Fraction 1, was colourless, and had b. p. 60—70°/11 mm.,  $D$  0.8643,  $n_D$  1.49143, which corresponds

with a terpene. It did not yield a solid nitrosite or dihydrochloride. Fraction II, b. p. 90—140°/11 mm., became colourless on boiling with sodium, and contained unchanged  $\alpha$ -gurjunene. Fraction III was intensely blue, but lost its colour on boiling with sodium. It contained a diterpene, b. p. 163—175°/13 mm.,  $D_{20}$  0.9495,  $n_D$  1.54135. The blue oil was free from nitrogen.

Cedrene and caryophyllene were also examined. In each case the molecular refraction of the lowest fraction indicated the presence of a terpene, the second fraction contained the unchanged sesquiterpene, and the final distillate agreed with a diterpene. Cadinene, however, a representative of the naphthalene type, was scarcely changed. The lowest fraction had b. p. 120—130°/vacuum,  $D$  0.9025,  $n_D$  1.50839,  $n_D - 7^\circ$ , and therefore contained practically no terpene, but chiefly a monocyclic sesquiterpene.

J. C. W.

Cadinene from *Daniella thurifera*. W. LENZ (*Ber.*, 1914, 47, 1989—1991).—So-called *Daniella thurifera* resin, a thin, blackish-brown balsam, can be separated, by distillation with steam, into an oil and a rather soft resin. The oil, which is free from phenolic substances, was fractionally distilled, when fractions were obtained with b. p. ranging from 120° to 290°. After treating with metallic sodium the three fractions obtained between 258° and 275° were again distilled, when two fractions, one colourless, b. p. 259—270°,  $D_{20}^\circ$  0.9850,  $n_D^{20}$  + 67.83°, the other bluish-green, b. p. 270—271°,  $D_{20}^\circ$  0.9845,  $n_D^{19}$  + 5.89° (tube, 0.2 cm.), were collected.

When these fractions were dissolved in an equal weight of ether and the solutions saturated in the cold with hydrogen chloride, an abundant crystalline deposit was obtained; after repeated recrystallisation from ethyl acetate, this solid was found to have m. p. 119° (corr.),  $[\alpha]_D^{25}$  - 39.82°, and to be identical with cadinene hydrochloride.

D. F. T.

Tobacco Resin. JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1914, i, 1196—1197; from *Fachliche Mitteilungen der österreich. Tabakregie*, 1913, 109—117).—Tobacco resin was thoroughly investigated about fifty years ago by Haid, but his results were not published, and were, in part, lost. A Kentucky tobacco was used, which, on extraction with alcohol, yielded a resin from which the resin acids were precipitated by lime. An essential oil was obtained by distillation with steam, whilst a neutral resin,  $C_{12}H_{20}O_2$ , remained, which was termed *kentuckyn*. Three acids were isolated from the calcium salts of the resin acids, namely, *kentuckylinic acid*,  $C_{28}H_{40}O_5$ , semi-solid, odourless; *kentuckynolic acid*,  $C_{22}H_{34}O_6$ , greenish-brown, soft, with an odour resembling honey, and *kentuckynic acid*,  $C_{22}H_{40}O_7$ , brown, very brittle, odourless. Haid's methods of separating these acids are unknown.

The author has employed the residues from certain Turkish tobaccos. The material is thoroughly extracted with warm water, and the dried material repeatedly treated with alcohol on the water-bath. After protracted cooling, the separated plant wax is removed and the alcohol distilled. Fatty acids are removed from the residue by treatment

with hot water. The yield of purified resin is about 250 grams from 7 kilograms of tobacco.

The dark grey resin is repeatedly warmed with five times its amount of ether. The insoluble portion is worked up according to (1) (see later). The soluble portion, after being partly freed from ether, is thoroughly agitated with 5% potassium hydroxide. The alkaline solution is extracted with ether to remove neutral resin. The portions soluble in ether are freed from nicotine and essential oil by distillation with steam in the presence of alkali. The residue remaining in the flask is *tabakoresen* (V). The saponifiable portions are separated by addition of solid potassium hydroxide and, after acidification, are dissolved in ether. Treatment with alkali also causes the saponification of a resin ester, the corresponding alcohol of which is less soluble in ether than the original ester and is therefore precipitated. By repeated solution and precipitation, the originally green precipitate becomes white (IV). The ethereal solution containing the resin acids is extracted with dilute alkali. Acidification with hydrochloric acid yields a mixture of acids which can be separated by lead acetate. The alcoholic solution of the resin acids is treated with an excess of lead acetate, whereby the lead salt of the  $\beta$ -acid (II) is separated as a dark green precipitate. The filtrate contains the  $\gamma$ -acid (III).

The following data are given for the pure products: I.  *$\alpha$ -Tobaccic acid*.—The brown resin which remains after extraction with ether is boiled in alcoholic solution, and the residue, after removal of alcohol, is dissolved in dilute alkali. Acidification of the hot solution precipitates the acid as a powder. It is a brittle, dark brown, odourless, amorphous substance, which is probably identical with Haid's kentucky nic acid. II.  *$\beta$ -Tobaccic acid* is isolated from the lead salt (see above) and forms a dark green, brittle mass which is probably contaminated with chlorophyll; it cannot be purified by means of its salts. (III.)  *$\gamma$ -Tobaccic acid* forms a viscous, brown liquid of unpleasant odour. It does not yield a lead salt. (IV.) *Tabakoresinol* can be obtained by the following process in addition to that previously given. The resin obtained by extraction with alcohol is warmed with water and powdered lime, and finally evaporated to dryness. By this treatment, the free and combined acids are converted into the corresponding calcium salts and the alcohol is liberated. The dry mass is extracted with ether to remove neutral resin, and the residue treated with boiling alcohol from which the resin alcohol separates on cooling. It forms white, microscopic needles, m. p. 213° (uncorr.). Analyses agree with the formula  $(C_8H_{10}O)_x$ . The *acetyl* derivative has m. p. 154°. (V.) *Tabakoresen*, both quantitatively and also as the odouriferous constituent, is the most important constituent of tobacco resin. In the concentrated condition it is a reddish-brown, viscous mass with an odour of honey. Dilute solutions are golden-yellow. It is not attacked by molten alkali. It has  $D_{18.7}^{20}$  0.941,  $n_D^{17}$  1.5169. It commences to boil at 230°, but decomposes and cannot be distilled unchanged under diminished pressure. Analyses and determinations of molecular weight lead to the formula  $(C_{19}H_{32}O)_x$ . (VI.) A small quantity of a pleasant smelling essential oil,  $n_D^{20}$  1.4882, is also obtained.

H. W.

**Resin Acids Soluble in Water from American Colophony.**  
LUDWIG PAUL (*Chem. Zentr.*, 1914, i, 1655—1656; from *Chem. Rev. Fett. Harz-Ind.*, 21, 5—8, 36—39, 53—56, 78—80).—American colophony can be separated by means of cold petroleum into a soluble and an insoluble portion. The latter is soluble, the former sparingly soluble, in dilute sodium hydroxide solution, and from the first-named solution the sodium salt of the chief resin acid (abietic acid) is deposited as a slimy precipitate. This is not, however, invariably the chief constituent of colophony, and may be a by-product, depending on whether large, glassy pieces or dust is employed. The acid is soluble in water or forms soapy emulsions; it is precipitated by hydrochloric acid as a curdy mass. The filtrate from the above sodium salt yields a second resin acid, which is readily soluble in sodium hydroxide solution, and does not dissolve in petroleum. The former contains a resinous impurity, which can be removed by repeated solution. A separation of the two chief constituents of colophony can therefore be effected by treatment with petroleum or sodium hydroxide, and the method can also be used for the identification of these constituents. The former acid cannot be completely separated from the latter by repeated solution in alcohol and sodium hydroxide and precipitation with hydrochloric acid. It appears, therefore, that the latter is continuously formed from the former, possibly in the same manner as a hydrate from its anhydride. Similarly, the complete conversion of the former acid into the latter cannot be accomplished. The best method of separating the constituents of colophony consists in treating the substance with twice its weight of petroleum. Large, glassy pieces yield 2%, dust yields up to 50%, of residue, which consists mainly of an acid soluble in water mixed with small quantities of the first acid.

*Distillation of Colophony-Petroleum Filtrates.*—The crude material is a viscous liquid, D ca 0.87. Above 320°, water is violently expelled and two distillates, named respectively light and heavy balsam, are obtained. The former when preserved deposits crystals, m. p. 150—160°, and are probably identical with Tschirch's  $\gamma$ -abietic acid (the substance is only present in small amount and does not appear to be characteristic of colophony). From the difference in the fractions obtained by the distillation of colophony and colophony-petroleum, the author is led to the conclusion that the former is a mixture of substances, whilst the products obtained by the aid of petroleum appear to be uniform. The acid which is soluble in petroleum (and can be obtained as a snow-white powder) has m. p. 74—75°, which rises after a lapse of time. On exposure to air, it forms increasingly large amounts of a residue insoluble in petroleum, probably by absorption of water. The crumbling of glassy pieces of colophony to dust is probably due to the same cause. The m. p. of the acid insoluble in petroleum is variable, generally above 100°.

Chemically, the acid soluble in petroleum resembles colophony. It is converted by washing with hydrochloric acid into the form soluble in water, and in this connexion the absorbed water appears to be particularly active. The behaviour is thus strongly reminiscent of starch.

The chief constituent of American colophony, the resin acid soluble in petroleum, is thus converted by water into a variety of substances, which, to a greater or less extent, exist originally in colophony. The cause of the phenomenon lies in the solubility of these substances in water through which the colophony gradually passes into solution and possibly suffers a degradation of its complex molecule. H. W.

**Mustard Oil Glucosides. IV. Phenylthiourethane-d-glucoside.** WILHELM SCHNEIDER and DOUGLAS CLIBBEN (*Ber.*, 1914, 47, 2218—2224).—The silver salt of phenylthiourethane reacts with acetobromoglucose in boiling xylene solution to form *tetra-acetylphenylthiourethane-d-glucoside*,  $\text{NPh}\cdot\text{COEt}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{O}_2\text{Ac}$ , which separates in colourless crystals, m. p.  $159^\circ$ ,  $[\alpha]_D^{20} = -2.46^\circ$ , in *s*-tetrachloroethane. As in the case of the corresponding aliphatic thiourethaneglucosides (this vol., i, 669), attempts to remove the acetyl groups and to obtain a crystalline glucoside were unsuccessful. Hydrolysis with baryta water yielded only phenylthiourethane and decomposition products of thioglucose. Alcoholic ammonia at room temperature, however, yielded acetamide and *phenylthiourethane-d-glucoside* as a dextro-rotatory syrup. The latter undergoes hydrolysis when left in aqueous solution, more quickly in acid solution, in two directions. On the one hand, phenylurethane and thioglucose are formed, as is the case with the aliphatic compounds, but, on the other hand, especially in acid solution, the products are phenylthiourethane and dextrose. The latter hydrolysis is met with in the case of the natural mustard oil glucosides, and the phenylthiourethaneglucoside therefore occupies an intermediate position between these and the aliphatic thiourethaneglucosides. Myrosin, however, is without influence on these synthetic glucosides.

When mixed with alcoholic silver nitrate solution, phenylthiourethane-d-glucoside gradually deposits the silver salt of thioglucose, and, on adding ammonia to the filtrate, the original silver salt of phenylthiourethane separates. The glucoside is therefore decomposed in two possible ways. The latter decomposition is in agreement with the formation of mustard oil silver sulphates from the natural glucosides. It is now also shown (following abstract) that thioglucose may be obtained from sinigrin, and, therefore, the relation between the above synthetic glucosides and the natural products is firmly established.

The silver salt of thioglucoside (*ibid.*) has been obtained in a purer form by dissolving the crude product in water, precipitating the metal by hydrogen sulphide, concentrating the filtrate in a vacuum, and adding slightly less than the required amount of ammoniacal silver nitrate. The compound forms snow-white flocks, m. p. about  $165^\circ$  (blackening), and is stable. A very slight excess of silver solution causes discoloration. J. C. W.

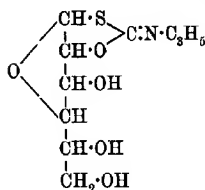
**Mustard Oil Glucosides. V. Constitution of Sinigrin.** WILHELM SCHNEIDER and FRITZ WREDE (*Ber.*, 1914, 47, 2225—2229).—When a solution of potassium methoxide is added to a hot methylalcoholic solution of sinigrin, potassium sulphate separates at once. On adding ammoniacal silver nitrate to the filtrate, the silver salt of



thioglucose is precipitated. This proves that the glucose molecule is attached to the sulphur atom in the glucoside, and the changes may be represented by the scheme:  $C_6H_5 \cdot N : C(O \cdot SO_3K) \cdot S \cdot C_6H_{11}O_5 \rightarrow C_6H_5 \cdot N : COMe \cdot S \cdot C_6H_{11}O_5 \rightarrow C_6H_5 \cdot N : C \cdot SH$ . The experience of the aliphatic thiourethaneglucosides has led Schneider to expect but little from attempts to isolate the methoxy-compound.

The above change is, however, not the only action of potassium methoxide on sinigrin, for, on precipitating the excess of silver from the filtrate from the above silver salt of thioglucose and evaporating the clear solution in a vacuum, a syrup remains which can be crystal-

lised from ethyl acetate. The product agrees with the formula  $C_{10}H_{15}O_5NS$ , and is called *merosinigrin*. It forms slender, colourless needles, m. p.  $192^\circ$ ,  $[\alpha]_D^{25} + 149.2^\circ$ , in water, and is very stable compared with sinigrin. It does not give a precipitate on boiling with alkaline lead solutions, nor does it reduce Fehling's solution, and it remains unchanged by 10% sulphuric acid at  $120^\circ$ . For these reasons, it is considered to be a ring condensation product of the annexed



formula, with which the formation of a *tri-acetyl* derivative, large colourless tablets, m. p.  $177^\circ$ , agrees. J. C. W.

**New Method of Converting Barbaloin into  $\beta$ -Barbaloin.** E. LÉGER (*Compt. rend.*, 1914, 158, 1903—1905. Compare this vol., i, 707).—On heating barbaloin with acetic anhydride and sodium acetate for an hour at  $100$ — $110^\circ$  it is converted into a penta-acetyl derivative, which is really a mixture of penta-acetylbarbaloin and penta-acetyl- $\beta$ -barbaloin. This mixture on saponification gives a yellow product soluble in a mixture of chloroform and methyl alcohol. The first crystals deposited from this solvent consist of barbaloin, but the mother liquors on evaporation yield  $\beta$ -barbaloin in the form of an amorphous powder. This substance, so prepared, does not undergo isomerisation under the influence of acetic anhydride. W. G.

**Production of Anthocyanins and Anthocyanidins.** ARTHUR ERNEST EVEREST (*Proc. Roy. Soc.*, 1914, [B], 87, 444—452).—Anthocyanin was obtained from yellow wallflower, yellow daffodil, white narcissus, yellow or white tulip, white primula, yellow crocus, yellow jasmin, primrose and lemon peel by reduction in the cold; no anthocyanidin is produced under these conditions, and no oxidation, after reduction, is necessary for the production of the anthocyanin pigment, unless the reduction is carried too far. N. H. J. M.

**Certain Reactions of the Colouring Matter of the Black-berry (Rubus Discolor).** GUIDO VECCHI (*Chem. Zentr.*, 1914, i, 1209; from *Staz. sperim. agrar. ital.*, 47, 60—64).—Determinations of the intensity of the colour show in 2% solution a cherry-red colour with a violet shade; in 1% solution, the colour is similar but weaker; in 0.5%

it is pure red; in 0.25% pink; in 0.05% solution it is colourless in thin layers, pale pink in a layer of 25 cms. The following experiments were effected with a solution of juice (50 c.c.) and water (250 c.c.). A dye is not extracted by light petroleum or ether from the acetic acid or sodium hydroxide solution. Amyl alcohol becomes dark violet, passing to carmine-red on addition of hydrochloric acid. The dye loses its violet tint on addition of mineral acids or acetic acid; nitric acid gives a golden-yellow, sodium or potassium hydroxide a dark green, ammonia or sodium carbonate a violet colour. Hydrogen peroxide is without action on the solution in hydrochloric acid; in alkaline solution it causes a colour change through brown to yellow. The acetic acid solution is decolorised by sodium hydrogen sulphite, but addition of an excess of sodium carbonate restores the wine-red colour.

*Lakes from the Dye of the Blackberry.*—Lead acetate gives a greyish-blue precipitate; silver nitrate has no action in the presence of acetic acid, but gives a chocolate-brown precipitate after addition of sodium carbonate. The filtrate becomes yellow on acidification. Barium chloride in the presence of sodium carbonate causes a grey precipitate, soluble in excess of acetic acid to a wine-red solution; copper acetate yields a bluish-black coloration, stable towards sodium carbonate and becoming red on addition of acetic acid. Alum and excess of sodium carbonate yield a violet-grey precipitate, and the blackish-violet filtrate becomes bright violet on addition of acetic acid. Zinc chloride yields a dark violet colour which becomes orange-yellow on addition of acetic acid. An excess of sodium carbonate precipitates a grey lake, and the filtrate is colourless. The precipitate is soluble in hydrochloric acid to a red solution, the colour of which can be extracted with amyl alcohol. Zinc chloride and a small amount of sodium hydroxide yield a greyish-violet precipitate which becomes yellowish-white on addition of an excess of alkali. The supernatant liquid is yellow. H. W.

**Crocetin.** FRITZ DECKER (*Arch. Pharm.*, 1914, 252, 139—160).—From analyses of its salts and molecular-weight determinations of its acetyl derivative, the author draws the conclusion that crocetin, the colouring matter of saffron, has the formula  $C_{10}H_{14}O_2$  (compare Kayser, A., 1885, 59). The ammonium salt,  $C_{10}H_{17}O_2N$ , crystallises from dilute alcohol in lustrous, red needles; the potassium, sodium, aniline, pyridine, and quinoline salts are also described. The acetyl derivative,  $C_{10}H_{18}O_2Ac$ , prepared by heating the potassium salt with acetyl chloride, crystallises in red needles, m. p. 174°. Crocetin combines with bromine in chloroform solution, yielding a dibromide, yellowish octahedra, m. p. 103—104° (decomp.), and must therefore contain one double linking. On oxidation with bromine in alkaline solution, it yields a compound,  $C_7H_{10}O_2Br_2$ , crystallising in colourless, felted needles. F. B.

**Lokao Dye.** ADOLF RÜDIGER (*Arch. Pharm.*, 1914, 252, 165—186).—Lokao or China green, a dye which has been entirely displaced by aniline greens, used to be extracted by the Chinese, from the bark of

the boughs and the roots according to some authorities, from the flowers and berries according to others, of *Rhamnus chlorophora* and *Rhamnus utilis*. The commercial product contains nearly 10% of moisture, and leaves 33.5% of ash, consisting chiefly of aluminium and calcium oxides. The author extracts the dye by the French process: solution in 2.5% ammonium carbonate, precipitation by alcohol, repetition of these operations until the ash-content is only 0.1% solution of the resulting ammonium salt in aqueous ammonium carbonate, and evaporation on the water-bath until crystals begin to separate. The substance thus obtained is *ammonium lokaonate*,  $C_{42}H_{46}O_{25} \cdot NH_4$  (a *di-ammonium* salt,  $C_{42}H_{44}O_{25}(NH_4)_2$ , can also be prepared), from which aqueous oxalic acid liberates lokaonic acid (Cloëz and Guignet's lokain),  $C_{42}H_{46}O_{25}$ , bluish-black substance with a metallic lustre. The acid is a rhamnoside, and its ammonium salt is decomposed by hot dilute sulphuric acid into lokanic acid and a sugar. The sugar, to which Kayser has given the name lokaose and the formula  $C_6H_{12}O_6$ , is proved to be rhamnose,  $C_6H_{12}O_6$ .

Lokanic acid (Cloëz and Guignet's lokaetin),  $C_{36}H_{38}O_{21}$ , is a violet-black, crystalline powder, and yields nitrophloroglucinol, m. p. 203–204°, by treatment with hot nitric acid, and phloroglucinol and delokanic acid by treatment with warm aqueous potassium hydroxide (1:1). Delokanic acid,  $C_{12}H_8O_6$ , contains one methoxy-group (as also does lokanic acid), but no hydroxyl groups, and is converted by nitric acid (D 1.4) into oxalic acid and a substance,  $C_8H_7O_5N$ , m. p. 129°, orange-yellow needles, which is possibly 2-nitro-5-methoxybenzoic acid (m. p. 132°). C. S.

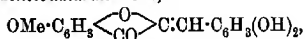
**Passage from Oxalacetic Ester to  $\alpha$ -Pyrone Derivatives.** H. GAULT (*Compt. rend.*, 1914, 159, 72–75. Compare A., 1913, i, 953; this vol., i, 384, 484).—Oxalocitrolactone, obtained by the lactonisation of oxalacetic ester (this vol., i, 484) on boiling with concentrated hydrochloric acid, yields oxalic acid, tricarballic acid, a chloro-compound, and an acid compound, m. p. 228°, which the author has shown to be 1:2-pyrone-6-carboxylic acid (compare Lapworth, T., 1901, 97, 1276). This compound is probably formed from oxalocitrolactone, by opening of the lactonic ring, followed by saponification, elimination of 2 molecules of carbon dioxide, dehydration, and subsequent cyclisation of the resulting oxalocrotonic acid. W. G.

**A New Flavone Synthesis.** H. SIMONIS (*Ber.*, 1914, 47, 2229–2233. Compare A., 1913, i, 890).—The chromones which were originally prepared by condensing phenols with esters of  $\beta$ -ketonic acids in the presence of phosphoric oxide happened to be new. The authors have therefore applied this new synthesis to the preparation of some chromones which other workers have obtained by other means. The method proved to be successful in the condensation of methyl methylacetoacetate and resorcinol to 7-hydroxy-2:3-dimethylchromone (Kostanecki and Lloyd, A., 1901, i, 735), a compound which sublimes in long, white needles, but failed in the case of ethyl acetoacetate and phenol. It was assumed that the latter ester is transformed almost entirely into the ketone in the presence of phenol, and, therefore, the

synthesis was modified by making use of the sodium derivative of the ester. This was fully justified, for the addition of phosphoric oxide to a suspension of ethyl sodioacetoacetate and phenol in toluene resulted in the formation of 2-methylchromone (Bloch and Kostanecki, A., 1900, i, 502). Flavone was also readily synthesised by adding alternately phosphoric oxide and ethyl sodiobenzoylacetate to a solution of phenol in xylene; the mixture being vigorously stirred and finally heated to 160° for two hours. J. C. W.

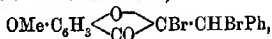
**Conversion of Benzylidenecoumaranones into Flavonols.** K. VON AUWERS and P. FOHL (*Annalen*, 1914, 405, 243—294).—The reaction whereby dibromobenzylidene-4-methylcoumaran-2-one is converted into 6-methylflavonol by hot alcoholic potassium hydroxide (Auwers and Müller, A., 1909, i, 45) proves to have only a limited applicability for the synthesis of flavonol derivatives, and unfortunately gives the worst results in the cases of the naturally occurring members.

The condensation of resorcinol dimethyl ether and chloroacetyl chloride by aluminium chloride and carbon disulphide yields *ω*-chloro-2-hydroxy-4-methoxyacetophenone,  $\text{CH}_3\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$ , m. p. 116°, colourless needles, which is converted into paeonol by reduction with zinc and glacial acetic acid. Blom and Tambor's so-called *α*-bromoessacetophenone dimethyl ether, prepared in a similar manner from bromoacetyl bromide and resorcinol dimethyl ether (A., 1905, i, 916), is shown to consist chiefly of the monomethyl ether, since it also yields paeonol by reduction. By boiling with alcohol and hydrated sodium acetate, *ω*-chloro-2-hydroxy-4-methoxyacetophenone yields 5-methoxycoumaran-2-one, m. p. 119—120°, colourless needles (described by Blom and Tambor [*loc. cit.*] as 3-methoxycoumaranone, m. p. 125°, yellow needles). At 50—60° in alcohol containing a little concentrated hydrochloric acid, 5-methoxycoumaranone condenses smoothly with protocatechualdehyde to form 3':4'-dihydroxy-3-methoxybenzylidenecoumaran-2-one,



m. p. 228—229° (decomp.), greenish-yellow needles (*diacetate*, m. p. 152—153°), and with vanillin to form 4'-hydroxy-3':5-dimethoxybenzylidenecoumaran-2-one, m. p. 195—195.5°, yellow rhombohedra (Blom gives m. p. 194°, brown leaflets), either of which reacts with methyl sulphate to form 3':4':5-trimethoxybenzylidenecoumaranone, m. p. 183—184° (Blom and Tambor give 189°).

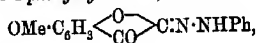
With the ultimate object of synthesising fisetin, the authors converted the preceding diacetate into its dibromo-additive compound; however, this and also the dibromide of 3':4':5-trimethoxybenzylidenecoumaranone proved to be too unstable to be converted into flavonol derivatives. The *dibromide*,



m. p. 191—192° (decomp.), of 5-methoxy-1-benzylidenecoumaranone is more stable than the two preceding dibromides and is converted in

boiling alcohol by *N*/10-sodium hydroxide into  $\alpha$ -bromo-5-methoxy-1-benzylidenecoumaran-2-one,  $\text{OMe}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{O}\\\text{CO}\end{smallmatrix}\rangle\text{C:PhBr}$ , m. p. 176—177°, yellow, pearly, hexagonal leaflets, and 7-methoxyflavonol in the ratio about 4:1; the acetate of 7-methoxyflavonol has m. p. 176° (Kostanecki gives 140°: A., 1904, i, 443).

The authors employ three criteria to differentiate between flavonols and the isomeric benzoylcoumaranones; the former (I.) have a higher m. p.; (II.) form in concentrated sulphuric acid yellow solutions with a blue fluorescence; (III.) do not yield characteristic derivatives with diazonium salts. The benzoate, m. p. 104—105°, long, colourless needles, of  $\omega$ -chloro-2-hydroxy-4-methoxyacetophenone, obtained in poor yield from the hydroxy-ketone and benzoyl chloride, is converted in benzene solution by prolonged boiling with potassium carbonate into 1-benzoyl-5-methoxycoumaran-2-one, m. p. 94—95°, yellow needles, which unlike the isomeric methoxyflavonol reacts with benzenediazonium chloride in very dilute alkaline solution to form 5-methoxycoumaran-1:2-dione-1-phenylhydrazine,



m. p. 248—249°, golden-yellow leaflets.

The dichlorides of benzylidenecoumaranones have been examined in the hope that they would be more stable than the dibromides. Unfortunately, mixtures of chlorinated products are obtained even with a molecular proportion of chlorine at 0°. By treatment with dry chlorine (6 mols.) in chloroform at 0°, 5-methoxy-1-benzylidenecoumaran-2-one yields 4-chloro-5-methoxy-1-benzylidenecoumaran-2-one

dichloride,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}\langle\begin{smallmatrix}\text{O}\\\text{CO}\end{smallmatrix}\rangle\text{CCl}\cdot\text{CHClPh}$ , m. p. 227—228°, colourless needles. Since a boiling alcoholic solution of this substance (and also of the corresponding dibromide) is converted into 6-chloro-7-methoxyflavonol, m. p. 197.5—198.5°, faintly yellow needles, by *N*/10-sodium hydroxide, whilst the unchlorinated analogue yields mainly  $\alpha$ -bromo-5-methoxy-1-benzylidenecoumaran-2-one by such treatment (see above), it is obvious that the nuclear chlorine atom facilitates the formation of the flavonol derivative, and the determination of its position is of great importance. This has been accomplished as follows: 5-Nitro-2-aminophenol is converted successively by the Sandmeyer reaction, by methylation, and by reduction into 6-chloro-*m*-anisidine, the solid diazonium sulphate of the latter is decomposed by dilute sulphuric acid at 150°, and the resulting 2-chloro-1-resorcinol methyl ether, b. p. 141—152°/13 mm. (once by chance a sample, m. p. 79—80°, has been obtained), is converted by methyl sulphate and warm alkali into 4-chlororesorcinol dimethyl ether, b. p. 135—137°/17—18 mm. This ether condenses with chloroacetyl chloride in the presence of aluminium chloride and carbon disulphide to form 5: $\omega$ -dichloro-2-hydroxy-4-methoxyacetophenone,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , m. p. 178.5—180°, colourless needles, which is also produced by the chlorination of  $\omega$ -chloro-2-hydroxy-4-methoxyacetophenone in chloroform. By boiling

with alcohol and hydrated sodium acetate, 5 :  $\omega$ -dichloro-2-hydroxy-4-methoxyacetophenone is converted into 4-chloro-5-methoxycoumaran-2-one,  $\text{OMe}\cdot\text{C}_6\text{H}_4\text{Cl}\langle\text{O}\rangle\text{CH}_2$ , m. p. 170—172° (decomp.), pale yellow needles, which condenses with benzaldehyde in alcohol containing a few drops of 8% sodium hydroxide at 50—60° to form 4-chloro-5-methoxy-1-benzylidenecoumaran-2-one, m. p. 172·5—173°, colourless or faintly yellow needles; the dibromide of the latter has m. p. 219°, and the dichloride, m. p. 227—228°, is identical with that obtained above by the chlorination of 5-methoxy-1-benzylidenecoumaran-2-one, and is converted into 6-chloro-7-methoxyflavonol by boiling alcohol and  $N/10$ -sodium hydroxide.

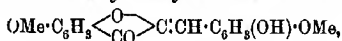
6-Chloro-7-methoxyflavonol is proved to be a flavonol, not the isomeric benzoylcoumaranone, by the three criteria mentioned above. 4-Chloro-1-acetyl-5-methoxycoumaran-2-one, m. p. 162—163°, colourless needles, prepared from the acetate, m. p. 93—94°, of 5 :  $\omega$ -dichloro-2-hydroxy-4-methoxyacetophenone for comparative purposes (the benzoyl derivative, which is isomeric with 6-chloro-7-methoxyflavonol, is very difficult to prepare), forms a greenish-yellow solution in concentrated sulphuric acid, and reacts with a benzenediazonium salt in very dilute alkaline solution to yield 4-chloro-5-methoxycoumaran-1 : 2-dione-1-phenylhydrazone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\text{Cl}\langle\text{O}\rangle\text{C}:\text{N}\cdot\text{NHPh}$ , m. p. about 215—220°, orange, crystalline powder.

The following substances are prepared by methods similar to those recorded above. The condensation of quinol dimethyl ether and chloroacetyl chloride in carbon disulphide on the water-bath yields only  $\omega$ -chloro-2-hydroxy-5-methoxyacetophenone, m. p. 81—81·5°, stout, yellow needles or irregular leaflets, when freshly prepared aluminium chloride is used, but results in the formation of a mixture of this substance and  $\omega$ -chloro-2 : 5-dimethoxyacetophenone, m. p. 87—88°, colourless needles, when stored aluminium chloride is employed.

4-Methoxycoumaran-2-one, m. p. 92·5—93·5°, flesh-coloured leaflets, forms a red solution in concentrated sulphuric acid; its aqueous solution exhibits a strong blue fluorescence.

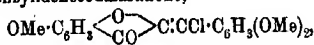
4-Methoxy-1-benzylidenecoumaran-2-one, m. p. 131—132°, yellow needles, forms a dibromide,  $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Br}_2$ , m. p. 142—143°, colourless needles, and a dichloride, m. p. 127—128°, colourless needles, which yield 50—60% and 80% respectively of 6-methoxyflavonol in the usual manner.

4'-Hydroxy-3' : 4-dimethoxy-1-benzylidenecoumaran-2-one,



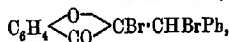
m. p. 160·5—161·5°, long, yellow needles, prepared from 4-methoxycoumaranone and vanillin, is converted by methyl sulphate and warm aqueous potassium hydroxide into 3' : 4' : 4-trimethoxy-1-benzylidenecoumaran-2-one, m. p. 171·5—172°, greenish-yellow needles. The action of chlorine on the trimethyl ether yields, according to the experimental conditions, a trichloro-derivative, m. p. 177—178°, a

substance, m. p. 215—216°, which is probably impure  $\alpha$ -chloro-3':4'-trimethoxy-1-benzylidenecoumaranone,

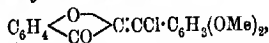


and a crude *dichloride*, m. p. 145—153°; from the last substance, 3':4':6-trimethoxyflavonol is obtained in 25% yield.

Benzylidenecoumaran-2-one forms a *dibromide*,



m. p. 147·5—148·5°, colourless needles, from which flavonol can be obtained in 32% yield. 4'-Hydroxy-3'-methoxy-1-benzylidenecoumaran-2-one, m. p. 203°, golden-yellow needles, prepared from coumaranone and vanillin, is converted by methylation into 3':4'-dimethoxy-1-benzylidenecoumaran-2-one, m. p. 159—160°, greenish-yellow needles. By chlorination (1 mol.) in chloroform at 0°, the dimethyl ether yields the *dichloride*, which, however, partly decomposes into  $\alpha$ -chloro-3':4'-dimethoxy-1-benzylidenecoumaran-2-one,



m. p. 211—212°, yellow needles, by crystallisation from alcohol or acetic acid. The *dibromide*, m. p. about 142°, pale yellow, crystalline powder, is somewhat more stable; it gives only a poor yield of 3':4'-dimethoxyflavonol.

1-Benzylidene-5-methylcoumaran-2-one, m. p. 153°, colourless, pearly leaflets, prepared from benzaldehyde and 5-methylcoumaran-2-one, forms a *dibromide*,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Br}_2$ , m. p. 153—154°, colourless needles, which is not unchanged by repeated crystallisation and is converted by boiling alcohol and *N*/10-sodium hydroxide (2 mols.) into a mixture of  $\alpha$ -bromo-1-benzylidene-5-methylcoumaran-2-one, m. p. 135—136°, yellow needles, and 7-methylflavonol, m. p. 160°, faintly yellow needles (acetate, m. p. 122—123°, colourless needles). The isomeric 1-benzoyl-5-methylcoumaran-2-one, m. p. 84—86°, rosettes of yellow needles, prepared from  $\alpha$ -bromo-1-benzylidene-5-methylcoumaran-2-one and sodium hydroxide in boiling aqueous alcohol, forms a yellow, non-fluorescent solution in concentrated sulphuric acid (the solution of 7-methylflavonol is yellow with a blue fluorescence) and reacts with benzenediazonium chloride in very dilute alkali to form 5-methyl-

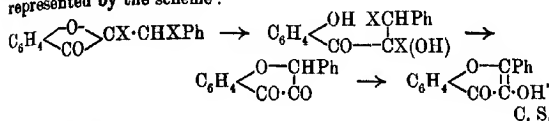
coumaran-1:2-dione-1-phenylhydrazine,  $\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C} : \text{N} \cdot \text{NHPH}$ ,

m. p. 230°, golden-yellow, pearly leaflets.

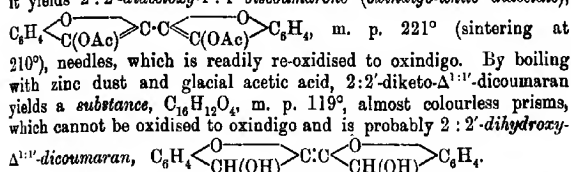
A survey of the preceding results shows that the production of a flavonol derivative is facilitated when the benzylidenecoumaranone dihaloid contains a methyl or methoxy-group or a chlorine atom in the para-position to the oxygen atom of the coumaranone ring, and is retarded by a methyl or methoxy-group in the meta-position, or by two methoxy-groups in the benzylidene nucleus.

Since dimethoxybenzylidenecoumaranone dihaloids readily lose hydrogen haloid with the formation of  $\alpha$ -haloiddimethoxybenzylidenecoumaranones, and also give poor yields of flavonol derivatives, the explanation of the formation of the latter advanced by Auwers and

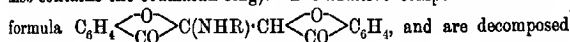
Müller (*loc. cit.*), which involves the intermediate production of  $\alpha$ -haloidbenzylidenecoumaranones, must be incorrect. It is shown experimentally that  $\alpha$ -haloidbenzylidenecoumaranones do not yield flavonols by treatment with dilute alkali. Consequently, a flavonol is produced from a benzylidenecoumaranone dihaloid only when the rupture of the coumaranone ring occurs more readily than the elimination of hydrogen haloid. Probably the course of the reaction is represented by the scheme:



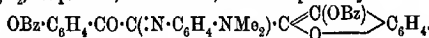
Oxindigo [2:2'-Diketo- $\Delta^{1:1'}$ -dicoumaran]. K. FRIES, A. HASSELBACH, and L. SCHRÖDER (*Annalen*, 1914, 405, 346—372). —2:2'-Diketo- $\Delta^{1:1'}$ -dicoumaran (oxindigo) (Fries and Hasselbach, A., 1911, i, 150) is extensively decomposed by alkaline reducing agents, but yields well-defined reduction products in acid solution. By reduction with zinc dust and boiling acetic anhydride, it yields 2:2'-diacetoxy-1:1'-biscoumarone (oxindigo-white diacetate),



In contrast to its nitrogen and sulphur isologues, 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran easily reacts additively with primary amines. (The only recorded case of a similar reaction in the series of indigoid dyes is that of gallorubin [Feuerstein and Brass, A., 1904, i, 344], which also contains the coumaran ring). The additive compounds have the



into their two generators by mineral acids. 1-Anilino-2:2'-diketo-1:1'-dicoumaran,  $\text{C}_{22}\text{H}_{15}\text{O}_4\text{N}$ , m. p.  $209^\circ$ , yellow needles, is prepared from oxindigo and aniline in boiling benzene. The additive compound with *p*-aminodimethylaniline, m. p.  $203^\circ$ , is identical with the condensation product of 2-coumaranone and 1-*p*-dimethylaminoanil-coumaran-1:2-dione (Fries and Hasselbach, *loc. cit.*). It is soluble in aqueous alcoholic sodium hydroxide without undergoing any profound change, and is recovered by acidifying the solution with acetic acid. By shaking the alkaline solution with benzoyl chloride, a substance,  $\text{C}_{28}\text{H}_{23}\text{O}_6\text{N}_2$ , m. p.  $220^\circ$ , is obtained, which is probably



This substance forms a red solution in concentrated sulphuric acid, which yields oxindigo and *p*-aminodimethylaniline by dilution with water, and is converted by a mixture of glacial acetic and concentrated

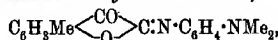


hydrochloric acids into *p*-aminodimethylaniline and a substance,  $C_{20}H_{18}O_7$ , m. p.  $148^\circ$ , yellow prisms, which doubtless has the formula  $OBz \cdot C_6H_4 \cdot CO \cdot CO \cdot C \begin{smallmatrix} \diagup COBz \\ \diagdown O \end{smallmatrix} C_6H_4$ , because its hydrolysis by sodium acetate yields oxindigo, and, moreover, as an  $\alpha$ -diketone the substance reacts with *o*-phenylenediamine to form a *quinoxaline*,  $C_{18}H_{12}O_5N_2$ , m. p.  $102^\circ$  (decomp.), greyish-yellow powder.

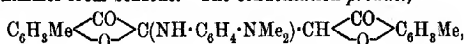
By heating with hydrogen chloride in glacial acetic acid in a sealed tube in the water-bath, 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran yields *o*-hydroxy-phenylglyoxylic acid and a substance,  $C_{16}H_{10}O_4$ , sintering at  $228^\circ$ , m. p.  $255^\circ$  (decomp.), dark red, metallic crystals, which is isomeric with, but apparently not nearly related to, the diketodicoumaran, forms a sodium salt,  $C_{16}H_9O_4Na$ , and *acetyl* derivative, m. p.  $242^\circ$ , red crystals, and is changed in boiling nitrobenzene into an isomeric substance,  $C_{16}H_{10}O_4$ , m. p.  $223^\circ$ , red crystals (*acetyl* derivative, m. p.  $153$ – $154^\circ$ , citron-yellow crystals).

2:2'-Diketo-5:5'-dimethyl- $\Delta^{1:1'}$ -dicoumaran,  $C_{18}H_{12}O_4$ , m. p.  $296^\circ$  (decomp.), stout, yellow needles, has been prepared from 5-methylcoumaran-2-one, and 4:4'-dichloro-2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran,  $C_{16}H_8O_4Cl_2$ , yellow crystals sintering at  $288^\circ$ , m. p.  $320^\circ$ , from 4-chlorocoumaran-2-one, by series of reactions quite similar to those whereby 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran is produced from 2-coumaranone (Fries and Hasselbach, *loc. cit.*).

1-*p*-Dimethylaminoanil-5-methylcoumaran-2-one,

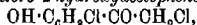


m. p.  $152^\circ$ , forms red crystals from alcohol or large prisms with bluish-black shimmer from benzene. The condensation product,



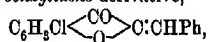
m. p.  $245^\circ$  (decomp.), reddish-brown needles, yields *p*-aminodimethylaniline and dimethyloxindigo by treatment with acetic and concentrated hydrochloric acids. Dimethyloxindigo is reduced to 2:2'-diacetoxy-5:5'-dimethyl-1:1'-dicoumarone, m. p.  $205^\circ$ , colourless needles, by zinc dust and acetic anhydride, and to 2:2'-dihydroxy-5:5'-dimethyl- $\Delta^{1:1'}$ -dicoumaran, m. p.  $172^\circ$ , faintly yellow prisms (*diacetals*, m. p.  $137^\circ$ ), by zinc dust and glacial acetic acid. By treatment with hydrogen chloride in glacial acetic acid at  $100^\circ$ , dimethyloxindigo yields 2-hydroxy-*p*-tolylglyoxylic acid and a compound,  $C_{18}H_{14}O_4$ , m. p.  $246^\circ$  (decomp.), dark red crystals.

*p*-Chlorophenol and chloroacetyl chloride react at  $130$ – $140^\circ$  to form *p*-chlorophenyl chloroacetate, m. p.  $36^\circ$ , b. p.  $181^\circ/45$  mm., which is converted into 5:5'-dichloro-2-hydroxyacetophenone,



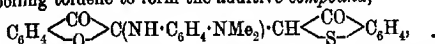
m. p.  $65^\circ$ , colourless needles, by aluminium chloride at  $140$ – $150^\circ$  and subsequent treatment with ice.

5:5'-Dichloro-2-hydroxyacetophenone is converted by boiling alcohol and hydrated sodium acetate into 4-chlorocoumaran-2-one, m. p.  $117^\circ$ , leaflets, which forms a *benzylidene* derivative,



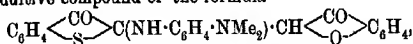
m. p. 169°, pale yellow needles. 4-Chloro-1-*p*-dimethylaminoanil-coumaran-2-one,  $\text{C}_6\text{H}_4\text{Cl} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p. 168–169°, forms red needles with a golden lustre. The condensation product, 4:4'-dichloro-2:2'-diketo-1-*p*-dimethylaminoanilino-1:1'-dicoumaran,  $\text{C}_6\text{H}_4\text{Cl} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{CH} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4\text{Cl}$ , m. p. 214° (decomp.), crystallises in brownish-red needles. C. S.

2-Thionaphthen-2-coumaroneindigo [Thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one]. K. FRIES and E. BARTHOLOMÄUS (*Annalen*, 1914, 405, 373–394).—Thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one (2-thionaphthen-2-coumaroneindigo),  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$ , sintering at 272°, m. p. 292°, red needles with a faint yellowish-green reflex, is prepared by a method quite analogous to that used in the preparation of 2:2'-diketo- $\Delta^{1:1'}$ -dicoumaran (preceding abstract). 1-*p*-Dimethylaminoanilicoumaran-1:2-dione and 3-oxythionaphthen react in boiling toluene to form the additive compound,

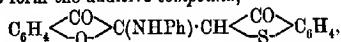


m. p. 220° (decomp.), reddish-brown needles; this substance, which is also produced from 2-coumaranone and thionaphthenquinone-*p*-dimethylamino-2-anil (Fummeier, A., 1910, i, 510), is decomposed into *p*-aminodimethylaniline and thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one by mineral acids.

The fact that the same additive compound is obtained in each of the preceding reactions, although the second method might be expected to yield an additive compound of the formula

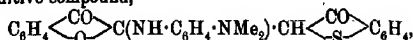


does not invalidate the explanation previously given of the course of the formation of oxindigo (preceding abstract) and similar indigoid dyes. The authors are of opinion that in all cases, where such dyes are prepared by methods similar to that here mentioned, the first product is an additive compound, which decomposes very rapidly into the indigoid dye and an amine; only in exceptional cases (oxindigo, preceding abstract; gallorubin, Feuerstein and Brass, A., 1904, i, 344) are such additive compounds stable. In this case, the two products of decomposition of the additive compound are thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one and *p*-aminodimethylaniline, which, however, readily unite, as is shown experimentally, to form the additive compound,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{CH} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$ , actually isolated. Thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2-one also combines with aniline to form the additive compound,



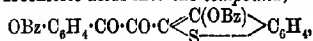
m. p. 170–173° (decomp.), ruby-red crystals, and is reduced by zinc dust and acetic anhydride to 3:2'-diacetoxythionaphthen-2:1'-coumarone  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OAc}) \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OAc}) \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p. 193°, colourless needles.

The additive compound,



is soluble in aqueous alcoholic sodium hydroxide, the *disodium* salt,  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_2\text{SNa}_2$ , brown needles, being formed. The *dimethyl ether*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{C} \begin{array}{c} \diagup \text{C(OMe)} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C}_6\text{H}_4$ , m. p.  $204^\circ$  (decomp.), reddish-yellow plates, and corresponding *dibenzoyl* derivative, m. p.  $204.5^\circ$ , brick-red, rhombic crystals, are prepared by the action of methyl sulphate and benzoyl chloride respectively on the alkaline solution.

The dibenzoyl derivative is converted by boiling glacial acetic and concentrated hydrochloric acids into the *compound*,

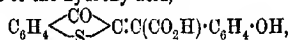


m. p.  $182^\circ$ , faintly yellow needles, and *p*-aminodimethylaniline; the former is converted into thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one by diluting its solution in concentrated sulphuric acid with water.

The *compound*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C}_6\text{H}_4$ , m. p.  $169^\circ$ , brownish-red needles, has been obtained (i) by hydrolysing the preceding dibenzoate,  $\text{C}_{30}\text{H}_{18}\text{O}_6\text{S}$ , by *N*/2-sodium hydroxide and boiling alcohol; (ii) from thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one in a similar manner, or by boiling it with glacial acetic and concentrated hydrochloric acids (by more prolonged heating, a *substance*, m. p.  $280^\circ$ , colourless prisms, is obtained), and (iii) synthetically from ethyl *o*-hydroxyphenylglyoxylate and 3-oxythionaphthen in the presence of boiling alcoholic sodium ethoxide. The compound reacts with *o*-phenylenediamine to form the *quinoxaline*,  $\text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ , m. p.  $263^\circ$  (decomp.), brownish-red needles, and is converted into thionaphthenquinone- $\Delta^{2:1'}$ -coumaran-2'-one by heating at about  $187^\circ$  or by solution in concentrated sulphuric acid. It is oxidised by alkaline potassium ferricyanide presumably to 3-oxythionaphthen-2-carboxylic acid and "thioindigo" is produced.

Coumaran-1:2-dione and 3-oxythionaphthen in glacial acetic acid at about  $80^\circ$  are converted by concentrated sulphuric acid into *thionaphthenquinone- $\Delta^{2:2'}$ -coumaran-1'-one*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C}:\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{O}$ ,

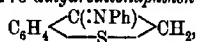
m. p.  $242^\circ$ , red needles, which forms a blood-red solution in aqueous-alcoholic sodium hydroxide; the solution becomes pale yellow when it is acidified by acetic acid, and yields the indigoid compound when it is acidified with concentrated hydrochloric acid. Doubtless the red and the yellow solutions contain respectively the disodium and the monosodium salts of the hydroxy-acid,



formed by the rupture of the lactone ring; the hydroxy-acid itself could not be isolated.

3-Oxythionaphthen and ethyl oxalate condense in the presence of alcoholic sodium ethoxide to form, after acidification, 3-hydroxythio-

*naphthen-2-glyoxylic acid*,  $C_8H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{S} \end{smallmatrix} C \cdot CO \cdot CO_2H$ , orange needles, m. p.  $173^\circ$  (decomp.), or yellow needles containing  $H_2O$ . It forms a violet solution in concentrated sulphuric acid, yields a *potassium salt*, citron-yellow needles, and *ethyl ester*, m. p.  $94^\circ$ , yellowish-brown needles, and reacts with boiling aniline to form oxanilide, the *anil*, m. p.  $179^\circ$ , brownish-yellow needles, of 3-hydroxythionaphthen-3-aldehyde, and 3-*keto-2:3-dihydrothionaphthen-3-anil*,



m. p.  $87^\circ$ .

C. S.

**Azomethines Derived from Phenylisooxazolone.** ANDRÉ METER (*Bull. Soc. chim.*, 1914, [iv], 15, 609—613).—An ineffectual attempt to prepare aminophenylisooxazolone by reduction of oximinophenylisooxazolone, and to oxidise it to a symmetrical rubazonic acid. Reduction of oximinophenylisooxazolone in dilute alcoholic solution with tin and hydrochloric acid yields benzylamine hydrochloride; the platinumchloride has m. p.  $197$ — $198^\circ$  (decomp.). Reduction with zinc and acetic acid produces benzonitrile and benzylamine, with a small proportion of a substance, probably aminophenylisooxazolone, which could not be isolated.

A. J. W.

**N-Demethylcodeine.** OTTO DIELS and ERNST FISCHER (*Ber.*, 1914 47, 2043—2047).—Ethyl azodicarboxylate combines quite generally with amines, producing colourless additive products (Diels and Fritzsche, A., 1911, i, 957; Diels and Paquin, A., 1913, i, 839), the hydrolysis of which offers a method for the dealkylation of amines; thus the crystalline additive compound of ethyl azodicarboxylate and dimethylamine on warming with dilute acids undergoes fission into ethyl *s*-hydrazinedicarboxylate, formaldehyde, and methylamine.

It has been found that such substances as methylpiperidine, atropine, morphine and codeine can be demethylated in this way, and the results with the last-named base are described.

Codeine readily condenses with ethyl azodicarboxylate in methylalcoholic or acetone solution, and the action needs to be moderated by cooling; the *additive* compound is a yellow, amorphous powder, which on warming with *N*-hydrochloric acid is resolved into formaldehyde, ethyl *s*-hydrazinedicarboxylate, and the hydrochloride of a substance,  $C_{11}H_{19}O_3N$ , designated *N-demethylcodeine*, derived from codeine by the removal of methyl from the nitrogen atom. *N*-Demethylcodeine forms small, hexagonal leaflets, m. p.  $185^\circ$ ; *hydrochloride*, needles, decomp. near  $314^\circ$ ; *diacetyl* derivative, needles (from benzene), m. p.  $176$ — $178^\circ$ .

D. F. T.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT (*Arch. Pharm.*, 1914, 252, 89—138).—A recapitulation and extension of previous work on the constitution of ephedrine and  $\psi$ -ephedrine (this vol., i, 78, and earlier abstracts).

On oxidation with potassium ferricyanide in alkaline solution, ephedrine yields benzaldehyde, ammonia and methylamine, together with *benzylidene-ephedrine*, which separates from ether in lustrous, long,

broad needles, m. p. 72—73°, and is also formed by the condensation of benzaldehyde and ephedrine in the presence of aqueous sodium hydroxide. The benzylidene compound yields a reddish-yellow, amorphous *platinichloride*, and a golden-yellow, microcrystalline *aurichloride*,  $2C_{17}H_{19}ON \cdot HCl \cdot AuCl_3$ . It is also formed by the oxidation of ephedrine with potassium permanganate or with chlorine and bromine in alkaline solution.

*Benzylidene-ψ-ephedrine*, obtained by the oxidation of ψ-ephedrine or by the direct condensation of benzaldehyde and ψ-ephedrine in the presence of aqueous sodium hydroxide, crystallises in transparent, tabular or leafy crystals, m. p. 65°, and forms a reddish-yellow *platinichloride*. Both the benzylidene compounds are readily resolved by warm hydrochloric acid into their components, and receive the following provisional constitution:



Although ephedrine and ψ-ephedrine readily undergo interconversion when heated with hydrochloric acid at 100°, their hydrochlorides remain unchanged when heated with water at 200—205°.

On distillation in an atmosphere of carbon dioxide, ephedrine and ψ-ephedrine hydrochlorides decompose into propiophenone, ammonia, methylamine and trimethylamine. When heated with phosphorus pentabromide, both bases are converted into α-bromo-β-methylamino-propylbenzene,  $CHPhBr \cdot CHMe \cdot NHMe$ , which forms a *hydrobromide*, crystallising in colourless, transparent leaflets or plates, m. p. 174° (decomp.); the *hydrochloride* also crystallises in leaflets or plates, m. p. 176—177°; the *platinichloride* forms small, lustrous, reddish-yellow leaflets, m. p. 188—189° (decomp.); the *aurichloride*, yellow leaflets, m. p. 138—139°.

The above-mentioned hydrobromide has  $[\alpha]_D^{20} - 92.54^\circ$  in aqueous solution, and  $- 92.79^\circ$  in alcoholic solution.

The rotation in aqueous solution gradually diminishes, and finally becomes positive, owing to the conversion of the bromo-hydrobromide into ψ-ephedrine *hydrobromide*, m. p. 179°, which is accompanied by a small amount of ephedrine *hydrobromide*, m. p. 205°.

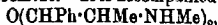
When heated with acetic anhydride the hydrobromide yields an *acetyl* derivative,  $CHPhBr \cdot CHMe \cdot CMeAc$ , crystallising in colourless columns, m. p. 175°,  $[\alpha]_D^{20} + 80.0^\circ$  in aqueous solution.

On treatment with silver nitrate in aqueous solution the acetyl derivative is converted into acetyl-ψ-ephedrine, which has m. p. 101—102° and forms a *platinichloride*.

β-Methylaminopropylbenzene,  $CH_3Ph \cdot CHMe \cdot NHMe$ , obtained by reducing the bromo-derivative (above) with zinc and hydrochloric acid, forms a *hydrochloride* (colourless, tabular crystals, m. p. 172°,  $[\alpha]_D^{20} + 19.14^\circ$  in aqueous solution), a *platinichloride* (reddish-yellow needles, m. p. 202°), and an *aurichloride*, crystallising in twisted needles, m. p. 126°; it is accompanied by methylamine and propylbenzene.

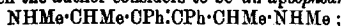
When kept for fifteen minutes in sulphuric acid solution at the ordinary temperature, both ephedrine and ψ-ephedrine give rise to the compound,  $\begin{matrix} CHPh \cdot O - SO_2 > O \\ | \\ CHMe \cdot NH_2Me \end{matrix}$ . This forms columnar or tabular, colour

less crystals, m. p.  $244^{\circ}$ ,  $[\alpha]_D^{25} + 109.09^{\circ}$  in aqueous solution, and is also obtained by the action of silver sulphate on  $\alpha$ -bromo- $\beta$ -methylamino-propylbenzene hydrobromide. It is accompanied by a compound,



which forms a *platinichloride*,  $C_{20}H_{28}ON_3 \cdot H_2PtCl_6 \cdot 3H_2O$  (small needles, m. p.  $225-227^{\circ}$ ), and an *aurichloride*,  $B_2HAuCl_4$ , lustrous needles, m. p.  $183-184^{\circ}$ .

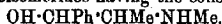
If the action of the sulphuric acid is continued for five days, ephedrine and  $\psi$ -ephedrine are converted into a yellow, amorphous substance, which the author considers to be an *apoeephedrine*,



the *aurichloride*, *platinichloride*, *dibromide* and additive compound with mercuric chloride are all amorphous.

On treatment with bromine in chloroform solution, ephedrine and  $\psi$ -ephedrine give rise to the corresponding hydrobromides.

The above results confirm the author's view that ephedrine and  $\psi$ -ephedrine are stereoisomerides having the constitution



F. B.

**Preparation of Double Halogen-hydracid Salts of Alkaloids of the Morphine Series.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 270575).—These double salts may be obtained by crystallisation from solutions containing equimolecular proportions of the separate salts, in presence or in absence of a precipitating agent. Descriptions are given of: *morphine narcotine hydrochloride*, short prisms, m. p. about  $200^{\circ}$ ; *codeine narcotine hydrochloride*, prisms, m. p.  $200^{\circ}$  (decomp.); and *morphine narcotine hydrobromide* ( $+ 2H_2O$ ), needles, sintering and turning brown at  $170^{\circ}$ .  
T. H. P.

**A Base,  $C_{13}H_9ON$ , from the Action of Aluminium Chloride on *o*-Nitrobenzyl Chloride and Benzene.** KARL DRECHSLER (*Monatsh.* 1913, 35, 533—560).—In the action of aluminium chloride on a mixture of benzene and *o*-nitrobenzyl chloride, a yellow solid, needles, m. p.  $169^{\circ}$ , is obtained as a by-product (Freund, A., 1897, i, 68); this substance, which gives solutions with a blue fluorescence, has the composition  $C_{13}H_9ON$ ; it gives a *hydrochloride*, pale yellow needles, m. p.  $169^{\circ}$  (decomp.), and a *mercurichloride*, golden-yellow leaflets, m. p.  $225-232^{\circ}$  (decomp.). Ebullioscopic determination of the molecular weight in benzene indicates that  $C_{13}H_9ON$  represents the molecular formula.

When treated in acetic acid solution with sodium nitrite solution, the above base does not appear to undergo diazotisation in the usual manner, for on the addition of water it is reprecipitated unchanged; the solution on warming, however, gives a substance,  $C_{13}H_{11}O_2N_2$  [possibly  $CO_2H \cdot C_6H_4 \cdot NPh \cdot N(OH)_2$ ], microscopic, yellow needles, m. p.  $365^{\circ}$ , which is soluble in solutions of alkalis, and on reduction by distillation with zinc dust, by sodium amalgam and alcohol or by tin and hydrochloric acid gives acridine or dihydroacridine. The action of nitrous

acid on the boiling alcoholic solution of the yellow base yielded a substance, yellow needles, m. p. 223—233° (possibly 10-hydroxyacridone).

The reduction of the yellow base,  $C_{13}H_9ON$ , by heating with zinc dust or by sodium amalgam and alcohol gave rise to acridine; attempts or acetylate the base by heating with acetic anhydride or acetic acid produced acridone, which was also obtained as a by-product in the action of nitrous acid on a hot solution of the base in hydrochloric or acetic acid. From these results the author draws the conclusion that the

yellow base is *N*-phenylanthranil,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NPh \end{smallmatrix}$ , which structure can be made to accord with the general behaviour of the substance.

The author discusses the probable method of formation of this substance and also of acridine, which is another by-product, in the original Friedel-Craft's reaction. A third by-product in the original synthesis is a colourless base,  $C_{13}H_9N$ , needles, m. p. 83°; *hydrochloride*, silky needles, m. p. 205—208°; *sulphate*, sparingly soluble; *acetyl derivative*, colourless needles, m. p. 212—213°; *mercurichloride*, yellow.

D. F. T.

**Preparation of 2-Phenylquinoline-4-carboxylic Acid.** CHEMISCHE FABRIK AUF ACTIEN (FORM. E. SCHERING) (Austrian Patent, 63525).—2-Phenylquinoline-4-carboxylic acid is obtained by the interaction of benzylideneaniline and pyruvic acid, this being effected by heating the condensation product of aniline and benzaldehyde with pyruvic acid in alcoholic solution.

T. H. P.

**Phenylloxindole.** R. STOLLÉ (*Ber.*, 1914, 47, 2120—2122).—Chloroacetodiphenylamide,  $CH_2Cl \cdot CO \cdot NPh_2$  (Frerichs, A., 1903, i, 610), when heated with aluminium chloride to 160—180° undergoes intramolecular condensation with the formation of *phenylloxindole*,

$C_6H_4 \begin{smallmatrix} \diagup CH_2 \\ \diagdown NPh \end{smallmatrix} > CO$ , colourless leaflets, m. p. 121°; *benzylidene derivative*,

yellow needles, m. p. 121°. Phenylisatin condenses with phenylloxindole in boiling acetic acid solution containing a little hydrochloric acid, the product being *diphenylisatinindigotin* (compare Wahl and Bayard, A., 1909, i, 330), reddish-brown needles, m. p. near 305°. It was not found possible to prepare phenylloxindole by heating *phenylisatin-hydrazone*, which was obtained in yellow needles, m. p. 192°, from the interaction of phenylisatin and hydrazine hydrate in boiling alcoholic solution.

*Chloroacetoethylaniilide*, m. p. 35°, b. p. 165°/21 mm., obtained from chloroacetyl chloride and ethylaniline in ethereal solution, when heated with aluminium chloride at 160° was gradually converted into ethylloxindole, needles, m. p. 97°.

The substance, m. p. 38°, obtained by Auwers and Arndt (A., 1909, i, 175) by the action of chloroacetyl chloride on *p*-thiocresol and described as *p*-thiocresyl chloroacetate,  $C_6H_4Me \cdot S \cdot CO \cdot CH_2Cl$ , is in reality *p*-tolylthiolacetyl chloride,  $C_6H_4Me \cdot S \cdot CH_2 \cdot COCl$ , and on hydrolysis yields *p*-tolylthiolacetic acid which is already known.

D. F. T.

**New Condensation Products of Carbazoles and Phthalic Anhydrides.** BADISCHE ANILIN- & SODA-FABRIK (Fr. Patent, 463508).—When carbazole or its derivatives substituted either at the nitrogen atom or in the nucleus are heated with phthalic anhydride or its derivatives in the presence of concentrated or slightly diluted sulphuric acid, condensation products are obtained which either are colouring matters or serve for the production of these. In certain cases, it is advantageous to submit the crude condensation products to subsequent treatment with a hypochlorite.

T. H. P.

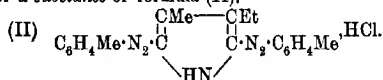
**Hæmopyrrole and the Scission of Hæmin by Oxidation.** AMANDUS HAHN (*Zeitsch. Biol.*, 1914, 64, 141—160).—A comprehensive review of the investigations into the oxidation products of hæmin, culminating in the synthesis of hæmatic acid (Küster and Weller, this vol., i, 442) and of the researches on the constituent pyrroles of hæmopyrrole oil. In connexion with the latter subject, the most recent paper under review is dated August, 1912, but important communications have since appeared (compare Fischer and Eismayer, this vol., i, 886).

J. C. W.

**Synthesis of Hæmopyrrole.** I. J. GRABOWSKI and L. MARCHELEWSKI (*Ber.*, 1914, 47, 2159—2161).—The authors give the term "hæmopyrrole I" to that constituent of crude hæmopyrrole which gives a red azo-dye with diazonium salts (A., 1912, i, 923), and has been shown to be 2-methyl-5-ethylpyrrole (compare also Piloty and Stock, A., 1912, i, 1015). The presence of this substance in hæmopyrrole renders necessary a revision of earlier discussions as to the nature of the latter substance (compare Fischer and Bartholomäus, A., 1912, i, 646).

2-Methyl-5-ethylpyrrole has now been synthesised by dry distillation of methylethylmaleinimide with zinc dust and calcium hydroxide in a current of carbon dioxide. The distillate was extracted with ether, and the solution treated with *p*-toluenediazonium chloride when a mixture of reddish-brown and blue crystals was obtained on evaporation. The latter, m. p. 252°, were separated by their much greater solubility in chloroform, and were found to consist of the substance (I), whilst the

former, (I) 
$$\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\overset{\text{CMe}\cdot\text{CEt}}{\underset{\text{NH}}{\text{C}}} \rightleftharpoons \text{C}\cdot\text{C} \begin{matrix} \text{CMe}\cdot\text{CEt} \\ \text{NH}\cdot\text{C}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me} \end{matrix} \cdot\text{HCl},$$
 which were needle-shaped, m. p. 256°, were of composition agreeing with that of a substance of formula (II),



Treatment of crude hæmopyrrole with *p*-toluenediazonium chloride gives two products agreeing in all respects with the synthetic substances described above.

D. F. T.

**The Constitution of the Blood and Bile Pigments.** III. HANS FISCHER and K. EISMAYER (*Ber.*, 1914, 47, 2019—2027. Compare Fischer and Bartholomäus, A., 1913, i, 209, 1236).—It is already known that formaldehyde will condense with substituted pyrroles, giving dipyrrolylmethane derivatives (Fischer and Bartholomäus, *loc.*

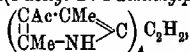


*cit.*; Piloty, Stock and Dormann, this vol., i, 755). The authors have therefore applied glyoxal in place of formaldehyde in the hope of obtaining tetrapyrrole derivatives.

Formaldehyde and hemopyrrole readily condense together when heated in alcoholic solution containing a little hydrochloric acid, the product being di(4:5-dimethyl-3-ethylpyrrol)methane, m. p. 108° (Piloty, Stock and Dormann, this vol., i, 327, give 99.5—100°); *picrate* needles, m. p. 186° (decomp.). Condensation of glyoxal with hemopyrrole under similar conditions gives rise to the same substance, which is not a leuco-compound but a dye, the *hydrochloride* (a red, crystalline solid with a green lustre) imparting a yellow colour to cotton.

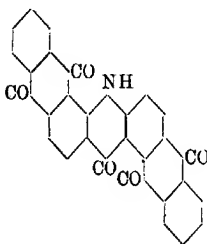
In a similar manner formaldehyde condenses with methyl phonopyrrolecarboxylate, the result being much less satisfactory if the free acid is used. The product is di(4:5-dimethyl-3-*o*-carboxymethylpyrrol)methane (for formula of free acid see Piloty, Stock and Dormann, *loc. cit.*). This substance, which was obtained in 50% yield from glyoxal and methyl phonopyrrolecarboxylate even in neutral solution, forms brownish-yellow crystals with a green lustre, m. p. 110—112°; *hydrochloride*, small rods with a greenish-red metallic lustre, soluble in chloroform to a deep red solution; *picrate*, m. p. 192° (decomp.). The constitution of this base was confirmed by molecular-weight determination in alcoholic solution and by its oxidation (with lead dioxide and sulphuric acid) and reduction (with a mixture of hydriodic and acetic acids) to hematic acid and phonopyrrolecarboxylic acid respectively. On warming with sodium methoxide solution, the compound was hydrolysed to the corresponding acid (compare Piloty, Stock and Dormann, *loc. cit.*)

The action of glyoxal on 3-acetyl-2:4-dimethylpyrrole follows a different course, *s-tetra*(3-acetyl-2:4-dimethylpyrrol)ethane,



being readily formed on the addition of a little hydrochloric acid to an alcoholic solution of these substances. This product, which is closely related to the non-isolated leuco-compound of Willstätter and Fischer's aetioporphylin (A., 1913, i, 1251), was obtained as the *hydrochloride*, prisms, decomp. at 210—225°. D. F. T.

**Diphthaloylacridones.** ALFRED ECKERT and OTTOKAR HALLA (*Monatsh.*, 1914, 35, 755—763).—1:2:6:7-Diphthaloylacridone



(annexed formula), red needles, is obtained directly and in almost quantitative yield by boiling 1-aminoanthraquinone-2-carboxylic acid, 2-chloroanthraquinone, sodium acetate, and a little cuprous chloride in nitrobenzene for fifteen hours. It forms a greenish-yellow solution in concentrated sulphuric acid, and the flocculent precipitate obtained by the addition of water readily yields a vat which dyes cotton reddish-yellow (in the massive state, the acridone forms a vat only with great difficulty).

The constitution of 1:2:6:7-diphthaloyl-

acridone is proved as follows. 3-Bromo-2-aminoanthraquinone, m. p. 307°, orange-yellow leaflets, prepared by boiling 1:3-dibromo-2-aminoanthraquinone, pyridine, and iron filings with glacial acetic acid, forms an acetyl derivative, m. p. 259°, almost colourless leaflets, and a benzylidene derivative, pale yellow leaflets. The latter condenses with 1-aminoanthraquinone-2-carboxylic acid under the conditions mentioned above to form a substance,  $C_{26}H_{18}O_6N_2$ , brownish-red, microscopic needles, by the hydrolysis of which is obtained 9-amino-1:2:6:7-diphthaloylacridone; by boiling the diazonium sulphate of this with alcohol, a diphthaloylacridone, identical with that described above, is obtained.

1-Aminoanthraquinone-2-carboxylic acid condenses with 1-chloroanthraquinone under the conditions described above to form 1:2:8:9-diphthaloylacridone, copper needles with a blue reflex.

Attempts to oxidise the methyl group in 2-methyl-1:2'-dianthrime have been unsuccessful. When the substance is fused with potassium hydroxide and lead oxide (compare D.R.-P. 192436) a product is obtained which is quite different from 1:2:6:7-diphthaloylacridone.

C. S.

**Preparation of Halogenated 5:5-Dialkylbarbituric Acids.** ALFRED EINHORN (D.R.-P. 272611).—When 5:5-dialkylbarbituric acids are heated with halogens under pressure, in some cases with addition of an indifferent organic diluent, they are converted into halogenated derivatives containing the halogens in the alkyl groups. These derivatives are soluble in dilute alkali carbonate or ammonia solution, from which they are precipitated unchanged by addition of acid.

Bromo-5:5-diethylbarbituric acid forms nodular masses of needles, m. p. 172—174°.

Dibromo-5:5-dipropylbarbituric acid forms needles, m. p. 176°.

Chloro-5:5-diethylbarbituric acid forms vitreous prisms, m. p. 199—200°.

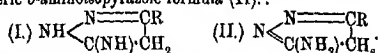
T. H. P.

**Incompatibility of Melubrin with Preparations which contain Aldehydes. Estimation of Aldehydes.** MARC TIFFENEAU (Chem. Zentr., 1914, i, 1368; from Bull. Sci. Pharmacol., 21, 71—73).—Melubrin,  $C_{11}H_{11}O_2N \cdot NH \cdot CH_2 \cdot SO_3Na \cdot H_2O$ , is gradually decomposed in aqueous solution into aminoantipyrine,  $C_{11}H_{11}O_2N \cdot NH_2$ , and sodium methanalsulphonate. For this reason its solutions give the same condensation products with aromatic aldehydes as aminoantipyrine itself. Anisylideneaminoantipyrine, piperonylideneaminoantipyrine, and vanillylideneaminoantipyrine have m. p.'s 168°, 229° and 198° respectively. This behaviour of melubrin renders it incompatible with preparations which contain aromatic aldehydes; on the other hand, it gives excellent results in the estimation of benzaldehyde and its homologues. For this purpose, two molecules of melubrin are required for each molecule of aldehyde. Condensation is effected in aqueous or feebly alcoholic solution. The condensation products are soluble in alcohol and are decomposed into their constituents by boiling dilute mineral acids.

H. W.

Bimolecular Nitriles. E. von MEYER (*J. pr. Chem.*, 1914, [ii], 90, 1—52).—A continuation of previous work (A., 1908, i, 909) on the properties and reactions of dinitriles,  $R \cdot C(NH) \cdot CH_2 \cdot CN$ .

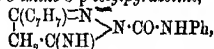
I. [With RICHARD FRIEDRICH].—*Derivatives of Iminopyrazoline and Aminopyrazole*.—Benzacetodinitrile and *p*-toluacetodinitrile react with hydrazine hydrate in alcoholic solution at 150–200°, yielding 5-iminopyrazolines (I), the salts of which are derived from the tautomeric 5-aminoisopyrazole formula (II):



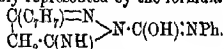
5-Imino-3-*p*-tolylpyrazoline (I,  $R = C_6H_4Me$ ), prepared from *p*-toluacetodinitrile, crystallises in white needles, m. p. 143°, and forms a hydrochloride, crystallising in pearly, lustrous leaflets, m. p. 253°. That the hydrochloride has the constitution represented in (II) ( $R = C_6H_4Me$ ) has been established by its behaviour towards nitrous acid. On successive treatment with sodium nitrite and sodium acetate in aqueous solution, it yields a very unstable, crystalline diazo-compound, which explodes when rubbed, or when heated at 121°. The diazonium chloride crystallises in light yellow needles, explodes at 157° without melting, and is remarkably stable in aqueous solution; it couples with  $\beta$ -naphthol in alcoholic solution, yielding an azo-dye, crystallising in yellowish-red needles, m. p. 237°.

5-Imino-3-*p*-tolylpyrazoline reacts with nitrous acid in alcoholic solution to form a reddish-brown, amorphous nitroso-compound, and with acetic anhydride at the ordinary temperature, yielding an *meso*-acetyl derivative,  $NaAc \begin{array}{c} \text{N}=\text{C} \cdot C_6H_4Me \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}) \cdot \text{CH}_2 \end{array}$ , felted, white needles, m. p. 221°. The diacetyl derivative,  $NaAc \begin{array}{c} \text{N}=\text{C} \cdot C_6H_4Me \\ \diagup \quad \diagdown \\ \text{C}(\text{NAc}) \cdot \text{CH}_2 \end{array}$ , white prisms, m. p. 163°, is obtained by heating the iminopyrazolone with an excess of acetic anhydride.

1-Phenylcarbonyl-5-imino-3-*p*-tolylpyrazoline,

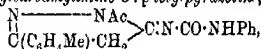


prepared from the iminopyrazoline and phenylcarbimide in hot xylene solution, crystallises in lustrous, silky, white needles, m. p. 173°, yields an *acetyl* derivative (slender needles, m. p. 161°), and when heated above its m. p. is converted into an *isomeride*, which separates from dilute alcohol as a micro-crystalline powder, m. p. 206°, and yields an *acetyl* derivative, m. p. about 204°. The constitution of the isomeride is probably represented by the formula



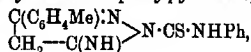
In agreement with this view, it is found that only the acetyl derivative of the less fusible isomeride is capable of yielding a *silver* salt on treatment with silver nitrate in alcoholic solution.

1-Acetyl-5-phenylcarbonylimino-3-*p*-tolylpyrazoline,



prepared by the interaction of phenylcarbimide and the monoacetyl derivative of 5-imino-3-*p*-tolylpyrazoline in benzene solution, crystallises in slender needles, m. p. 177°, and is isomeric with the preceding acetyl derivatives.

1-Phenylthiocarbamyl-5-imino-3-*p*-tolylpyrazoline,



obtained by heating the iminopyrazoline with phenylthiocarbimide, crystallises in stout prisms, m. p. 196°.

The hydrochloride of 5-imino-3-*p*-tolylpyrazoline reacts with benzene-diazonium chloride in aqueous solution, yielding 5-imino-3-*p*-tolyl-4-

pyrazolonephenylhydrazone,  $\text{NH} \begin{array}{c} \text{N} \\ \text{C}(\text{NH}) \cdot \text{C} \cdot \text{N} \cdot \text{NHPh} \end{array}$  which crystal-

lises in golden-yellow needles, m. p. 233°, forms a yellow *silver* salt, and yields in hydrochloric acid solution a *diazo*-compound which couples with resorcinol to form a brown *azo*-dye.

1-Carbamyl-5-imino-3-*p*-tolylpyrazoline,  $\begin{array}{c} \text{C}(\text{C}_6\text{H}_4\text{Me})\text{:N} \\ | \\ \text{CH}_2-\text{C}(\text{NH}) \end{array} > \text{N} \cdot \text{CO} \cdot \text{NH}_2$

obtained in the form of its *hydrochloride* by the interaction of semicarbazide hydrochloride and *p*-toluoacetodinitrile in alcoholic solution, crystallises in white leaflets, m. p. 186°, and is hydrolysed by hydrochloric acid to 5-imino-3-*p*-tolylpyrazoline.

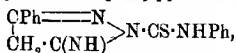
5-Imino-3-phenylpyrazoline (I. above, R = Ph), prepared from benzoacetodinitrile and hydrazine hydrate, separates from alcohol in lustrous, pearly leaflets, m. p. 119°, and forms a *hydrochloride*, which can be diazotised and is, therefore, derived from the tautomeric 5-amino-3-phenylisopyrazole (II. above, R = Ph); the *diazonium chloride* explodes at 98°, and couples with resorcinol, yielding a reddish-yellow *azo*-dye.

On treatment with nitrous gases in boiling glacial acetic acid solution, 5-imino-3-phenylpyrazoline yields an amorphous, reddish-brown

*nitrosoacetyl* derivative,  $\begin{array}{c} \text{N} \cdot \text{N} \cdot \text{Ac} \\ | \\ \text{CPh} \cdot \text{CH}_2 \end{array} > \text{C} \cdot \text{N} \cdot \text{NO}$ . With acetic anhydride

it forms a *diacetyl* derivative, white needles, m. p. 151°, and a *monoacetyl* derivative, stout prisms, m. p. 162°, which forms a white *silver* salt.

1-Phenylthiocarbamyl-5-imino-3-phenylpyrazoline,



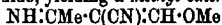
prepared by heating the iminophenylpyrazoline with phenylthiocarbimide at 100°, has m. p. 187°.

II. [With P. ESSER.]—*Condensation of Dinitriles with Esters.*—

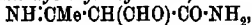
Under the influence of sodium or potassium ethoxide, dinitriles condense with the ethyl esters of formic, phenoxyacetic, and oxalic acids, yielding compounds of the type  $\text{NH} \cdot \text{CR} \cdot \text{CH}(\text{CN}) \cdot \text{COR}$ , where R = H,  $\cdot \text{CH}_2 \cdot \text{OPh}$ , and  $\cdot \text{CO}_2\text{Et}$  respectively.

$\beta$ -Imino- $\alpha$ -formylbutyronitrile,  $\text{NH} \cdot \text{CMe} \cdot \text{CH}(\text{CHO}) \cdot \text{CN}$ , prepared by condensing ethyl formate with acetodinitrile by means of potassium ethoxide in ethereal solution, and acidifying the aqueous solution of

the resulting *potassium* salt, has m. p. 109°. The *potassium* salt reacts with methyl iodide, yielding a *methyl ether*,



(long needles, m. p. 40°), and when kept in aqueous solution is slowly hydrolysed to  $\beta$ -*imino- $\alpha$ -formylbutyramide*,

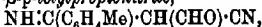


which separates from alcohol in needles, m. p. 269°.

$\alpha$ -*Formyl- $\beta$ -phenyliminobutyronitrile*,  $\text{NPh}\cdot\text{CMe}\cdot\text{CH}(\text{CHO})\cdot\text{CN}$ , obtained from *N*-phenylacetodinitrile and ethyl formate in a similar manner, has m. p. 102°.

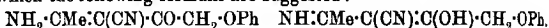
$\beta$ -*Imino- $\alpha$ -formyl- $\beta$ -phenylpropionitrile*,  $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CHO})\cdot\text{CN}$ , from benzoacetodinitrile, crystallises in needles, m. p. 106°, and is readily hydrolysed to the corresponding amide; the *potassium* salt yields, with methyl iodide, a *methyl ether*,  $\text{NH}\cdot\text{CPh}\cdot\text{C}(\text{CN})\cdot\text{CH}\cdot\text{OMe}$ , having m. p. 84°.

$\beta$ -*Imino- $\alpha$ -formyl- $\beta$ -p-tolylpropionitrile*,



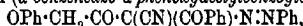
prepared from *p*-tolylacetodinitrile, has m. p. 122°, and forms a *phenylhydrazone*, m. p. 188°; on treatment with benzenediazonium chloride and sodium acetate in alcoholic solution, it is converted into a yellow *azo*-compound ( $\alpha$ -*benzenesazo- $\alpha$ -formyl- $\alpha$ -p-toluylacetonitrile*), m. p. 120°,  $\text{C}_6\text{H}_5\text{Me}\cdot\text{CO}\cdot\text{C}(\text{CHO})(\text{CN})\cdot\text{N}\cdot\text{NPh}$ . Ethyl phenoxyacetate readily condenses with acetodinitrile in ethereal solution in the presence of *potassium* ethoxide, yielding  $\beta$ -*imino- $\alpha$ -phenoxyacetylbutyronitrile*, m. p. 96°,  $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , together with an *isomeride*, m. p. 123°, which constitutes the main product of the reaction. The more fusible  $\alpha$ -*isomeride* is present in the condensation product in the form of its *potassium* salt, and is isolated by extraction with water and subsequent acidification with hydrochloric acid.

The insoluble residue consists of the less fusible  $\beta$ -*isomeride*, for which the following formulæ are suggested:



In agreement with the first formula it is found that the  $\beta$ -*isomeride* does not form a *potassium* salt.

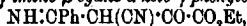
Benzoacetodinitrile and ethyl phenoxyacetate give rise to  $\beta$ -*imino- $\alpha$ -phenoxyacetyl- $\beta$ -phenylpropionitrile*,  $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , which also exist in two isomeric forms. The  $\alpha$ -*isomeride* has m. p. 87°, and is present in the condensation product in the form of its *potassium* salt; on treatment with benzenediazonium chloride it is converted into an *azo*-compound ( $\alpha$ -*benzenesazo- $\alpha$ -phenoxyacetylbenzoylacetonitrile*),



which crystallises in golden-yellow leaflets, m. p. 110°. The  $\beta$ -*isomeride* has m. p. 114°, and constitutes the main product of the reaction.

*p*-Toluoacetodinitrile yields  $\beta$ -*imino- $\alpha$ -phenoxyacetyl- $\beta$ -p-tolylpropionitrile*,  $\text{NH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , which was isolated in only one (the  $\beta$ -) form, having m. p. 148°. Ethyl  $\gamma$ -*imino- $\beta$ -cyano- $\alpha$ -ketovalerate*,  $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , prepared from acetodinitrile and ethyl oxalate, has m. p. 90° and is readily hydrolysed to the corresponding *acid*, m. p. 168°, an aqueous solution of which, on acidification with hydrochloric acid, slowly deposits  $\gamma$ -*imino- $\alpha$ -keto*

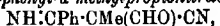
*β*-carbamylvaleric acid, m. p. 268°,  $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . The silver and ammonium salts of the two last-named acids are mentioned. Ethyl *γ*-imino-*β*-cyano-*α*-keto-*γ*-phenylbutyrate,



obtained in the form of its potassium salt from benzoacetodinitrile and ethyl oxalate, has m. p. 90°, and on treatment with ammonia in ethereal solution yields the corresponding amide, m. p. 199° (decomp.); the potassium salt is hydrolysed in acid solution to *γ*-imino-*α*-keto-*β*-carbamyl-*γ*-phenylbutyric acid,  $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , m. p. 259°.

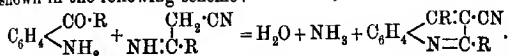
The following compounds were prepared from *p*-toluoacetodinitrile in a similar manner: *γ*-imino-*β*-cyano-*α*-keto-*γ*-*p*-tolylbutyric acid, white needles, m. p. 283°; ethyl ester, m. p. 142°, and amide, slender needles, m. p. 206°. Both the acid and ester are hydrolysed by boiling aqueous sodium hydroxide to oxalic acid and *β*-imino-*β*-*p*-tolylpropionamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , which has m. p. 177°, acid is also obtained by heating *p*-toluoacetodinitrile with alcoholic potassium hydroxide.

*β*-Imino-*α*-formyl-*β*-phenyl-*α*-methylpropionitrile,



prepared from benzopropiondinitrile and ethyl formate in the presence of potassium ethoxide, crystallises in leaflets, m. p. 133°, and forms a yellowish-white potassium salt.

III. [With G. HAENSEL].—Derivatives of *β*-cyanoquinoline.—*o*-Aminobenzaldehyde, *o*-aminoacetophenone, and isatic acid undergo condensation with dinitriles, yielding derivatives of 3-cyanoquinoline, as shown in the following scheme:



3-Cyano-2-phenylquinoline-4-carboxylic acid, prepared by heating benzoacetodinitrile with isatic acid in alcoholic solution in the presence of zinc chloride, crystallises in slender, white needles, m. p. 267—268°.

3-Cyano-2-*p*-tolylquinoline-4-carboxylic acid, obtained in a similar manner from *p*-toluoacetodinitrile, forms white prisms, m. p. 215°.

When heated in glacial acetic acid solution at 150°, *o*-aminoacetophenone and acetodinitrile yield 3-cyano-2:4-dimethylquinoline, which crystallises in white needles, m. p. 161—162°, yields a picrate (yellow needles, m. p. 203°), and is hydrolysed by concentrated hydrochloric acid at 180° to 1:4-dimethylquinoline-3-carboxylic acid, white needles, m. p. 231°, and the corresponding amide, small needles, m. p. 198°; the acid yields a hydrochloride, which forms prismatic crystals, and is readily hydrolysed by water.

3-Cyano-2-phenyl-4-methylquinoline, prepared from benzoacetodinitrile and *o*-aminoacetophenone in a similar manner, crystallises in long, white needles, m. p. 166—167°; 2-phenyl-4-methylquinoline-3-carboxylic acid forms white needles, m. p. 284—285° (decomp.); the amide crystallises in clusters of needles, m. p. 189—190°.

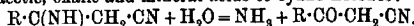
3-Cyano-2-*p*-tolyl-4-methylquinoline crystallises in yellow needles, m. p. 133°.

When heated at 120°, *o*-aminobenzaldehyde condenses with aceto-

dinitrile, yielding 3-cyano-2-methylquinoline, white needles or prisms, m. p. 131°.

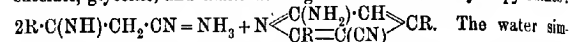
3-Cyano-2-phenylquinoline, prepared from benzoacetodinitrile and o-aminobenzaldehyde in alcoholic solution at 180°, forms white needles, m. p. 193—194°, and is hydrolysed by hydrochloric acid to 2-phenylquinoline-3-carboxylic acid, small needles, m. p. 230° (decomp.).

IV. [With P. BERGE, R. OEHLER, and E. SCHLETTER].—Action of Various Acids on Dinitriles. In aqueous solution dinitriles are hydrolysed by acetic, oxalic and mineral acids to cyano-ketones:

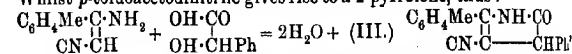


The action has been quantitatively followed in the case of acetodinitrile, benzoacetodinitrile, and *p*-toluoacetodinitrile by determining the diminution in the concentration of the acid. It is found that acetodinitrile is much more readily hydrolysed than the two remaining nitriles, the rates of hydrolysis being in the ratio 30:4:7 in the order given.

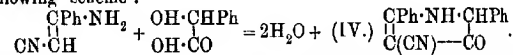
The interaction of dinitriles and anhydrous organic acids depends on the nature of the acid and nitrile, and also on the conditions under which the reaction is carried out. Cyanoacetic, α-hydroxyisobutyric, succinic, glycollic, and malic acids give rise to aminocyanopyridines:



The water simultaneously produced by the action of the ammonia on the acid may lead to a partial or complete displacement of the amino-group by hydroxyl. If the reaction is carried out in alcoholic solution, displacement of the amino-group by the ethoxy-group may also take place. A remarkable difference in the behaviour of benzoacetodinitrile and *p*-toluoacetodinitrile towards mandelic acid has also been observed. Whilst *p*-toluoacetodinitrile gives rise to a 2-pyrrolone, thus:



benzoacetodinitrile is converted into a 3-pyrrolone, as shown in the following scheme:



When heated with anhydrous cyanoacetic acid at 140°, acetodinitrile yields 6-amino-3-cyano-2:4-dimethylpyridine, which is accompanied by a substance,  $C_{13}H_{10}O_2N_2$ , crystallising in needles, m. p. 220°; if the components are not anhydrous, 3-cyano-6-hydroxy-2:4-dimethylpyridine is produced.

The action of succinic acid on *p*-toluoacetodinitrile in alcoholic solution at 150° leads to the formation of 3-cyano-6-hydroxy-2:4-di-*p*-tolylpyridine,  $N \begin{array}{c} \diagup C(OH) \text{---} CH \\ \diagdown C(C_6H_4Me) : C(CN) \end{array} \diagup C \cdot C_6H_4Me$ , m. p. 265°, together with a small amount of 6-amino-3-cyano-2:4-di-*p*-tolylpyridine, m. p. 165°, which forms a picrate, m. p. 205°.

When heated with glycollic acid in alcoholic solution, benzoacetodinitrile is converted into 3-cyano-6-ethoxy-2:4-diphenylpyridine, slender needles, m. p. 141—142°; if the reaction is carried out in a sealed tube at 150°, the ethoxy-derivative is accompanied by 6-amino

3-cyano-2:4-diphenylpyridine, which crystallises with  $\frac{1}{2}$ H<sub>2</sub>O in needles, m. p. 213°, and yields a deep yellow *picrate*.

3-Cyano-6-hydroxy-2:4-diphenylpyridine, prepared by heating benzoacetodinitrile with  $\alpha$ -hydroxyisobutyric acid in alcoholic solution at 150°, crystallises in lustrous, silky needles, m. p. 192°, with previous sintering at 143°.

The above-mentioned 3-cyano-6-ethoxy-2:4-diphenylpyridine is converted by the action of hydrochloric acid at 200° into 6-hydroxy-2:4-diphenylpyridine, which crystallises in slender needles, m. p. 208°.

4-Cyano-3-phenyl-5-p-tolyl-2-pyrrolone (formula III above), prepared by heating *p*-toluoacetodinitrile and mandelic acid in equimolecular proportions in alcoholic solutions at 150°, forms slender needles, m. p. 200°, with previous softening at 150°. It yields a yellow *picrate*, and when heated with hydrochloric acid at 200° is transformed into 3-phenyl-5-p-tolyl-2-pyrrolone,  $\text{NH} \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_5, \text{Me})\text{CH} \\ \text{CO} \text{---} \text{CHPh} \end{smallmatrix}$ , slender, white needles, m. p. 235—237°.

The interaction of benzoacetodinitrile and mandelic acid under similar conditions leads to the formation of 4-cyano-2:5-diphenyl-3-pyrrolone (formula IV above), which crystallises from alcohol in white needles, m. p. 230°, with previous softening at 200°, and yields an *acetyl* derivative (pale yellow prisms, m. p. 134°), a *phenylhydrazine*, slender, grey needles (decomp. 260°), and an *oxime*, crystallising in pale yellow needles, which decompose above 170° without melting.

When heated with concentrated hydrochloric acid at 200°, the cyanodiphenylpyrrolone is converted into 2:5-diphenyl-3-pyrrolone, white needles, m. p. 205°. It is hydrolysed by alcoholic potassium hydroxide to 4-carbamyl-2:5-diphenylpyrrolone,  $\text{NH} \begin{smallmatrix} \text{CHPh}\cdot\text{CO} \\ \text{CPh}=\text{C}\cdot\text{CO}\cdot\text{NH}_2 \end{smallmatrix}$ , which crystallises in small prisms, m. p. 255° (decomp.).

4-Cyano-5-phenyl-2-methyl-3-pyrrolone,  $\text{NH} \begin{smallmatrix} \text{CPh}=\text{C}\cdot\text{CN} \\ \text{CHMe}\cdot\text{CO} \end{smallmatrix}$ , prepared from lactic acid and benzoacetodinitrile, forms small needles, m. p. 170° (decomp.), yields an *acetyl* derivative, m. p. 185° (decomp.), and when heated with hydrochloric acid is transformed into 5-phenyl-2-methyl-3-pyrrolone, pale yellow needles, m. p. 215°, with partial decomposition.

Attempts to condense benzoacetodinitrile with oxalic acid in alcoholic solution at 100° resulted in the formation of  $\omega$ -cyanoacetophenone; at 170°, 3-cyano-6-hydroxy-2:4-diphenylpyridine is produced.

F. B.

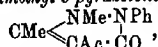
Preparation of 2- or 3-Antipyrilquinoline-4-carboxylic Acids. FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 270487).—These compounds, obtained by the interaction of 4-acetyl-1-phenyl-2:3-dimethylpyrazolone or its homologues with isatin in alkaline solution, show the actions both of 1-phenyl-2:3-dimethyl-5-pyrazolone and of the quinoline-4-carboxylic acids and find therapeutic application.

2-Antipyrilquinoline-4-carboxylic acid, m. p. 266—268°, and



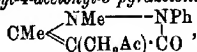
3-antipyryl-2-methylquinoline-4-carboxylic acid or 2-methylantipyryl-quinoline-4-carboxylic acid, m. p. 238—239°, are described.

4-Acetyl-1-phenyl-2:3-dimethyl-5-pyrazolone,



obtained by the action of acetyl chloride on 1-phenyl-2:3-dimethyl-5-pyrazolone in presence of ammonium chloride, forms colourless crystals, m. p. 150—151°, and gives a red coloration with ferric chloride in aqueous solution.

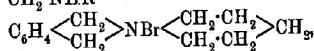
1-Phenyl-2:3-dimethyl-4-acetonyl-5-pyrazolone,



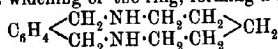
m. p. 87°, gives a red coloration with ferric chloride in aqueous solution and is obtained by the action of chloroacetone and sodium hydroxide on 1-phenyl-3-methyl-5-pyrazolone and methylation of the 1-phenyl-3-methyl-4-acetonyl-5-pyrazolone thus obtained. T. H. P.

The Interaction of Bicyclic Ammonium Compounds and Secondary Cyclic Bases. The Stereochemistry of Tervalent Nitrogen. M. SCHOLTZ (*Ber.*, 1914, 47, 2162—2170).—It is known from the earlier work of the author that *o*-xylylene bromide reacts with secondary amines, giving rise to substituted ammonium bromides

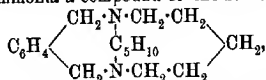
of the type  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{NRR}'\text{Br}$ , which on heating with ammonia produce bases with two secondary amino-groups as indicated by the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{NHR} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{NHR}' \end{array}$ . With the product,



obtained from *o*-xylylene bromide and piperidine, the action of ammonia causes a widening of the ring, forming a structure



(A., 1898, i, 305, 383, 471, 565, 567). By allowing xylenepiperidinium bromide to react with piperidine a compound was obtained to which the structure  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NC}_5\text{H}_{10})_2$  was ascribed, but if the behaviour of xylenepiperidinium bromide towards piperidine is the same as towards ammonia a compound of the structure



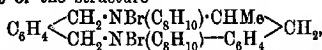
might be expected. A decision between these two alternative formulæ by direct methods is not easy, but with compounds of an analogous nature, the occurrence of isomerism has been observed, which is explicable only by the latter representation (compare Scholtz and Wolfrum, A., 1910, i, 771).

In the same manner as piperidine, 2-methyldihydroindole reacts with *o*-xylylene bromide in the presence of alkali hydroxide in hot alcoholic solution, giving *o*-xylylene-2-methyldihydroindolium bromide,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{NBr} \begin{array}{c} \text{CHMe} \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$ , colourless, tetragonal prisms (with  $\text{H}_2\text{O}$ , from water), which melts in its water of crystallisation at  $135-140^\circ$ , and, after re-solidifying, melts again at  $207^\circ$ ; the anhydrous substance crystallises from a mixture of chloroform and ether in hexagonal tablets; the more sparingly soluble *iodide*, obtained by precipitation from the bromide by potassium iodide, forms stellar aggregates of needles, m. p.  $220^\circ$ ; the *chloride*, obtained from the bromide by the action of silver chloride, forms hexagonal tablets, m. p.  $210^\circ$ .

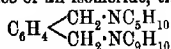
When the above bromide is heated with aqueous ammonia for 48 hours at  $200^\circ$  in a sealed tube, *propylenephénylene-o-xylylenediamine*,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{NH} \cdot \text{CHMe} \\ \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \end{array} \text{CH}_2$ , is obtained as an almost colourless, viscous oil, b. p.  $250-255^\circ/16$  mm., with slight decomposition. The presence of two secondary amino-groups in this substance was confirmed by treating with *o*-xylene bromide and alkali hydroxide when a bromide of the structure

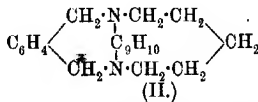
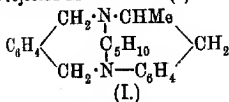


colourless prisms, m. p.  $112^\circ$ , was obtained, and was converted by successive treatment with silver oxide and chloroplatinic acid into the *platinichloride*, orange-yellow needles, m. p.  $177^\circ$  (decomp.).

2-Methyldihydroindole, when heated for eight hours at  $200^\circ$  with *o*-xylylenepiperidinium bromide in alcoholic solution, gave rise to ( $\alpha$ ) *o*-xylylenepiperidyl-2-methyldihydroindyl, colourless needles, m. p.  $87^\circ$  (*dimethiodide*, colourless needles, m. p.  $173^\circ$ , with decomp.), for which, on account of the existence of an isomeride, the structure



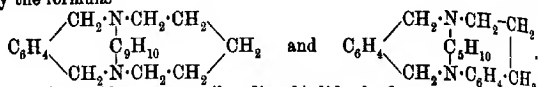
is rejected in favour of (I).



When *o*-xylylene-2-methyldihydroindolium bromide and piperidine were heated together in the presence of water, an *isomeride* ( $\beta$ ) of the preceding substance was obtained in colourless prisms, m. p.  $102^\circ$ ; this is a strong, reducing agent, liberating silver from silver nitrate in the presence of acetic acid; it forms a *methiodide*, tablets, m. p.  $200^\circ$ ; *perchlorate*, sparingly soluble prisms, m. p.  $182^\circ$ . Both the  $\alpha$ - and  $\beta$ -isomerides give deep red solutions in nitric acid. The existence of isomerism is attributed to the situation of the three valencies of trivalent nitrogen in one plane, one of the isomerides possessing the structure represented by formula (I), whilst the other may be represented by formula (II).

In an analogous manner to the preceding, tetrahydroquinoline reacts with *o*-xylylenepiperidinium bromide in the presence of alcohol at  $200^\circ$ , giving  $\alpha$ -*o*-xylylenepiperidyltetrahydroquinolyl, whilst the  $\beta$ -isomeride was produced by the interaction of *o*-xylylenetetrahydroquinolinium

bromide, colourless needles, m. p. 233° (previously described as an oil, Scholtz and Wolfrum, *loc. cit.*), and piperidine in the presence of water at 200°. The existence of these isomerides is again explained by the formula



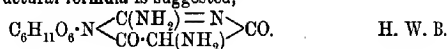
The  $\alpha$ -isomeride was an oil; *dimethiodide*, leaflets, m. p. 78°; *picrate*, orange-yellow needles, m. p. 116–117°. The  $\beta$ -isomeride forms colourless prisms, m. p. 89°; *methiodide*, stellar aggregates of needles, m. p. 206°; *perchlorate*, rhombic tablets, m. p. 196°.

The isomerism in each case was confirmed by molecular-weight determination. It is remarkable that, not only do the isomerides differ in physical properties but also in chemical, the  $\alpha$ -isomerides behaving as di-acid bases, whilst the  $\beta$ -compounds are only mon-acid. All these bases exceed brucine in their sensitiveness towards nitric acid, giving an intense red coloration even in dilute solution, a similar effect being also produced by other oxidising agents.

D. F. T.

**Vicine.** P. A. LEVENE (*J. Biol. Chem.*, 1914, 18, 305–311).—The author supplements the work of Johnson and Johns on this compound (this vol., i, 366, 579). Crystalline vicine obtained from vetch meal has m. p. 242° and  $[\alpha]_D^{20} - 11.7^\circ$ . On heating at 100° with 20% sulphuric acid, divicine sulphate,  $\text{C}_8\text{H}_{12}\text{O}_6\text{N}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , appeared as a crystalline deposit. The compound differed from the sulphates of 4:5-diamino-tetrahydropyrimid-2:6-dione and of 2:5-diaminotetrahydropyrimid-4:6-dione, both of which were prepared by Traube's method (A., 1900, i, 416); but it is regarded as more closely allied to the latter than to the former, because of its behaviour towards nitrous acid and urea (uric acid formation).

After the removal of the divicine sulphate, dextrose was recognised in the filtrate, and vicine is therefore regarded as a nucleoside composed of 2:5-diaminotetrahydropyrimid-4:6-dione and dextrose. The following structural formula is suggested,



**The Diketotriazines.** J. BOUGAULT (*Compt. rend.*, 1914, 159, 83–85).—The author has prepared a number of diketotriazines of

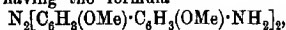
the type  $\text{R} \cdot \text{C} \begin{array}{c} \diagup \text{N} \text{---} \text{NH} \diagdown \\ \diagdown \text{CO} \text{---} \text{NH} \diagup \end{array} \text{CO}$  by the action of warm dilute alkali on the semicarbazones of the corresponding  $\alpha$ -ketonic acids, the reaction being  $\text{R} \cdot \text{C} \begin{array}{c} \diagup \text{N} \text{---} \text{NH} \diagdown \\ \diagdown \text{CO} \cdot \text{H} \cdot \text{NH}_2 \diagup \end{array} \text{CO} = \text{H}_2\text{O} + \text{R} \cdot \text{C} \begin{array}{c} \diagup \text{N} \text{---} \text{NH} \diagdown \\ \diagdown \text{CO} \text{---} \text{NH} \diagup \end{array} \text{CO}$ .

The diketotriazines are crystalline substances, insoluble in water, but soluble in alcohol. Their melting points are much higher than those of the corresponding semicarbazones, and they can often be sublimed unaltered. They are acid, and on titration in alcoholic solution with phenolphthalein as indicator they behave as monobasic acids. They yield alkali salts and alkyl derivatives. The monoalkyl

derivatives obtained by the action of the monopotassium salts on alkyl iodides are crystalline, have lower melting points than the diketotriazines, and are more soluble in organic solvents. They also exhibit slight acidity towards phenolphthalein. The dialkyl derivatives are similarly prepared and have lower melting points than the monoalkyl derivatives. Alkalis decompose the monoalkyl derivatives, giving the corresponding alkylamines. The following diketotriazines have been prepared: *diketodimethylethyltriazine*,  $\text{CMe}_2\cdot\text{C}_2\text{H}_5\text{O}_2\text{N}_3$ , m. p.  $285^\circ$ ; *diketophenyltriazine*,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_3\text{Ph}$ , m. p.  $262^\circ$ ; *diketop-methoxyphenyltriazine*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5\text{ON}_3$ , m. p.  $273^\circ$ ; *diketobenzyltriazine*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_5\text{O}_2\text{N}_3$ , m. p.  $208^\circ$ ; *diketophenylethyltriazine*,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_5\text{O}_2\text{N}_3$ , m. p.  $266^\circ$ ; *diketopiperonalethyltriazine*,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_8\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_5\text{O}_2\text{N}_3$ , m. p.  $282^\circ$ .

The method appears to be general, except for the fact that all attempts to prepare diketomethyltriazine (compare Thiele and Bailey, A., 1899, i, 169) in this way were unsuccessful. W. G.

**Quinonoid Oxidation Products of Dianisidine and their Polymerisation.** JAMES MOIR (*South African J. Sci.*, 1914, March).—By the rapid addition of a slight excess of concentrated aqueous ferric chloride to a solution of dianisidine in an excess of dilute hydrochloric acid below  $25^\circ$ , a substance,  $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_4\text{Cl}_2$ , bluish-black crystals, is immediately and almost quantitatively obtained, which is regarded as the hydrochloride of the quinhydrone of dianisidine and the unknown 3:3'-dimethoxydiphenylquinonedi-imine. The corresponding *hydrobromide*,  $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_4\text{Br}_2$ , purple crystals, basic *nitrate*,  $\text{C}_{28}\text{H}_{31}\text{O}_4\text{N}_4(\text{NO}_3)$ , violet-black paste, *sulphate*,  $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_4(\text{SO}_4)$ , almost black substance, and *dichromate*,  $\text{C}_{28}\text{H}_{30}\text{O}_4\text{N}_4\cdot 2\text{H}_2\text{Cr}_2\text{O}_7$ , blackish-violet cake, are described. These salts yield dianisidine by reduction with stannous chloride, undergo various colour changes by treatment with water and with acids, and yield by treatment with alkalis or aqueous ammonia, dianisidine and a base,  $\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_4$ , m. p.  $220\text{--}240^\circ$ , dark brick-red substance. The base yields only dianisidine by reduction with hot stannous chloride, and forms olive basic salts and purple acid salts. The author regards it as a polymerised, 3:3'-dimethoxydiphenylquinonedi-imine having the formula



and suggests that Willstätter and Kalb's diphenylquinonedi-imine (A., 1905, i, 361) has a similar constitution. An attempt to prepare 3:3'-dimethoxydiphenylquinonedi-imine by oxidising dianisidine in chloroform by lead peroxide resulted in the formation of the base,  $\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_4$ , together with a small amount of a higher polymeride,  $\text{C}_{48}\text{H}_{42}\text{O}_6\text{N}_6(?)$ , m. p.  $245^\circ$ . C. S.

**The Direct Fixation of Metals by Proteins.** A. BENEDICENTI and S. REBELLO-ALVES (*Biochem. Zeitsch.*, 1914, 65, 107—116).—A preliminary account is given of the solvent action of serum and egg-albumin on finely divided iron. This action takes place when all the carbon dioxide which can be removed by a pump has been eliminated, and also when the serum has been submitted to prolonged dialysis. The action is not a new suspension phenomenon, and the iron taken

up is partly masked. Various possible explanations of the action are offered by the authors. S. B. S.

**Composition of the Insoluble Gases Formed by the Decomposition of Organic Substances.** R. H. JESSE (*Chem. Zentr.*, 1914, i, 1682; from *University of Illinois, Bulletin*, 1912, 9, 47—61).—A gas explosion in a sewer has caused the author to compare the composition of the gas with that formed in other reservoirs. Methane was present to the extent of 85% in the sewer, compared with 70—73% in the reservoir. When compared with the figures of other investigators, the composition of the gases is shown to vary within wide limits, particularly with regard to nitrogen and carbon dioxide. The origin of the gases is to be found in the hydrolysis of proteins, which are peptonised and also converted into amino-acids, leucine, tyrosine and aromatic compounds. Gas is not evolved at this stage. Further, the amino-acids are converted into fatty or aromatic acids with formation of nitrogen and ammonia. The acids obtained by the decomposition of protein substances are transformed into simpler acids with evolution of hydrogen and methane. Carbamide is converted into carbon dioxide and ammonia, which is transformed into the carbonate; cellulose evolves carbon dioxide and hydrogen or methane, and yields fatty acids. Butyric and lactic acids are formed from starch and sugar, whereby, also, carbon dioxide, hydrogen and water are produced. In addition, fats undergo aerobic decomposition, and hydrogen sulphide and mercaptan are produced from organic sulphur compounds. H. W.

**Influence of the Mineralisation of the Caseins on their Solubility.** L. LINDER (*Compt. rend.*, 1914, 159, 122—124. Compare A., 1913, i, 1116, 1414).—The soluble caseins of colostrum contain less inorganic salts than those of milk. The soluble caseins of milk contain from 4.61—8.36% of phosphoric acid and from 7.22—14.97% of lime, whilst those of colostrum contain only from 0.6—1.4% of phosphoric acid and from 0.37—1.49% of lime. Further, the solubility of the caseins in milk serum, or even in water, is greater when they contain less mineral matter. W. G.

**The Conjugated Sulphuric Acid from Tendonucoid.** P. A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1914, 18, 237—240. Compare A., 1913, i, 917, 1006).—The analysis of the conjugated sulphuric acid obtained from tendonucoid shows that the components of this acid are identical with those of chondroitin-sulphuric acid, namely, chondrosamine, and glycuronic, acetic and sulphuric acids. Since the ratio of nitrogen to carbon was also 1:14, and the substance contained only one acetyl group in its molecule, the identity of the conjugated sulphuric acid from tendonucoid with that of chondroitin-sulphuric acid from cartilage is regarded as established. The melting point of the glycuronic acid osazone hydrazide obtained from either substance should be 122° (decomp.) instead of 115° as previously reported. H. W. B.

The Chemistry of Proteolytic Ferments. E. HERZFELD (*Biochem. Zeitsch.*, 1914, 64, 103—105).—By dialysing a certain quantity of pepsin in aqueous solution, a definite amount of substances yielding the ninhydrin reaction is obtained in the dialysate. When dialysed in 0.18% hydrochloric acid, less of such substances are obtained. The same phenomenon is observed in the case of peptones. The degrading action of pepsin in water and 0.18% hydrochloric acid is about the same. Peptone solution, both in water and in acid, also degrades proteins to the same extent in both solutions, but the peptone must be derived from the same protein as the substrate; thus, a peptone from egg-albumin will degrade this protein, whereas silk pepton<sup>8</sup> will not. Trypsin in aqueous solution on dialysis gives in the dialysates substances yielding the ninhydrin reaction, but less of these are obtained from trypsin when dissolved in sodium carbonate. Trypsin will degrade proteins more rapidly in the presence of carbonates than in pure water. The same happens in the case of amino-acids, which degrade proteins; in this case the specificity is not so marked as in that of the peptones. On the ground of these experiments, the author puts forth the theory that pepsin owes its action to the peptones it contains, and trypsin to the amino-acids, and as peptones and amino-acids can act catalytically (in traces) in degrading proteins, there is no ground for regarding pepsin and trypsin as ferments. Similar generalisations are made with regard to other ferments.

S. B. S.

The Conditions of Action of Pepsin. L. MICHAELIS and A. MENDELSSOHN (*Biochem. Zeitsch.*, 1914, 65, 1—15).—The optimal hydron concentration for peptic activity is about  $4 \times 10^{-2}$ . Salts cause a small transference of this point toward the less acid position. Pepsin is a ferment which follows the ordinary dissociation laws, and the free cation is the proteolytically active constituent. This peptic activity can still be detected when the hydron concentration reaches  $10^{-5}$ , and from this point onwards the precipitating (rennin) action increases, and the pepsin in an electric field wanders to the anode. These facts seem to indicate that the rennet action of pepsin is due to the anion. There is no evidence of a special casease which digests the casein clot in a medium which is only very slightly acid.

S. B. S.

Ferments. I. Estimation of Fermentative Change by means of the Interferometer. I. Application of the "Interferometric Method" to the Study of Protective Ferments. PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1914, 91, 440—449).—In experiments such as Abderhalden's test for pregnancy the activity of the protective ferments leads to the formation of peptones which dissolve in the serum. The author's method for detecting such changes is to measure by means of the interferometer the change in concentration which occurs in the serum in consequence of the solution in it of the peptones.

R. V. S.

Mechanism of Oxidative Changes. III. HEINRICH WIELAND (*Ber.*, 1914, 47, 2085—2111. Compare A., 1913, i, 1304).—In the

last communication, it was shown that certain typical biological oxidations are really processes of dehydrogenation; in other words, the catalytic action of the ferments concerned does not consist in an activating of oxygen, but rather in such an activating of the hydrogen atoms involved, that they are readily taken up by appropriate "acceptors."

The behaviour of aldehydes in presence of ferments is of especial interest. Three types of reactions have been recognised, namely, oxidation of the aldehyde, accelerated reduction of a third substance, such as methylene-blue or *p*-benzoquinone, and intramolecular redistribution of the aldehyde into the corresponding acid and alcohol. It is considered that these processes can be explained by the action of a single ferment, a "dehydrase," and that the assumption of separate oxydases, reductases, and mutases is therefore unnecessary. The aldehyde reacts in the form of its hydrate, and the ferment activates two of the hydrogen atoms, which are then taken up by an "acceptor." This may be oxygen or methylene-blue, etc., or it may be the non-hydrated aldehyde, which would account for the mutase action, thus,  $R\cdot CH(OH)_2 + R\cdot CHO = R\cdot CO_2H + R\cdot CH_2\cdot OH$ . What the end result may be, whether it manifests itself as an oxidation or reduction or "mutation" or a mixture of these effects, depends on the concentration and speed of reaction of the various "acceptors." These conclusions are illustrated quantitatively in the case of Schardinger's milk ferment and salicylaldehyde.

In the first place, when salicylaldehyde and fresh, unboiled milk are left in an atmosphere of nitrogen, salicylic acid and saligenin are formed. In air or oxygen, more acid and less alcohol are formed, since the oxygen competes with the aldehyde-anhydride as an "acceptor" of the activated hydrogen of the aldehyde-hydrate. In presence of methylene-blue, in an atmosphere of nitrogen, still less alcohol is formed, the speed at which the dye takes up the hydrogen being much greater than in the case of oxygen. Against the assumption that all these effects are to be referred to the action of one ferment on salicylaldehyde, two objections may be raised, both of which have been answered. In the first place, it is necessary to show that salicylic acid and saligenin themselves are not affected by the ferment, in the presence of air or methylene-blue, which is, indeed, the case. Then it might be argued that a ferment specific to, say, the mutase action, would be damaged or destroyed by the presence of, say, methylene-blue. It is well known that the milk enzyme soon becomes inactive and this is especially so in the presence of the aldehyde, oxygen, or methylene-blue. A kinetic study of the above reactions shows, however, that the decrease in activity follows the same course in each case. This would not be expected if three different enzymes were at work, and is, therefore, evidence in support of the "dehydrase" theory.

Further studies were made on the influence of the concentration of the aldehyde on the reactions. The effect on the reaction depends, not only on the speed at which the aldehyde is activated, this being raised by increased concentration, but also on the speed at which the "acceptor" combines with the hydrogen. The mutase effect in a

nitrogen atmosphere is considerably influenced, but not so the oxidation in oxygen, since this gas acts very slowly as an "acceptor." It is therefore possible, under certain conditions of concentration, that more salicylic acid will be formed in nitrogen than in oxygen. Methylene-blue, however, acts as an "acceptor" about eight times as fast as oxygen, so the reduction of the dye is considerably accelerated by raising the concentration of the aldehyde, within certain limits.

Reference must be made to the original for details of the very many experiments. Underlying them all, was the separation and estimation of salicylic acid and saligenin. For this purpose, the warm mixture was treated with 4*N*-sulphuric acid and left overnight. An aliquot part of the filtrate from the casein (usually 150 c.c.) was shaken with 120, 100, 80, and then 50 c.c. of ether, and the extract was dried and concentrated to 5 c.c. in a 30 c.c. bottle. The unchanged aldehyde was then removed as the bisulphite compound and the salicylic acid was extracted from the ethereal solution by sodium hydrogen carbonate, and the saligenin by sodium hydroxide. The respective aqueous solutions were decomposed by sulphuric acid, extracted with ether, and the extracts were dried and evaporated. The substances were obtained pure enough to weigh, but their purity was controlled by titration. For the estimation of saligenin, an approximately 0.4% solution was treated with an excess of 0.2—0.3*N*-bromine water, and, after twenty seconds, the excess was determined iodometrically. Under these conditions, a constant amount of 5.38 equivalents of bromine is absorbed by saligenin. It is extremely difficult to recover the whole of these compounds from milk, but 60—65% of the acid and 90% of the alcohol may be regularly separated by the above method. J. C. W.

**Mineral Water and Catalysis. Action of Philothion on Treatment with Water from Sulphur Springs.** J. DE REX-PAILHADE (*Chem. Zentr.*, 1914, i, 1210; from *Bull. gén. Thérap.*, 1913, No. 18, 8 pp. Compare A., 1906, i, 999).—The rôle of hydrogenating ferments and the specific action of the sulphur in waters from sulphur springs on philothionic hydrogen are discussed. Hydrogen sulphide is formed in the stomach by the action of the sulphur of the gastric juice on the water, and, occasionally, separation of free sulphur occurs. The latter, in contact with the philothion of the epithelial cells, forms hydrogen sulphide, which is added to that derived from the decomposition of sulphides. The hydrogen sulphide passes rapidly into the circulation, and, in a more oxidising medium, is converted into water and free sulphur, the latter being very finely divided or, possibly, in colloidal or atomic form. The sulphur is carried by the blood into all the organs, and again combines with philothionic hydrogen to yield hydrogen sulphide, whilst the philothionic hydrogen is regenerated by abstraction of hydrogen from the food. The cycle of operations is continuously repeated, and thus the philothionic hydrogen behaves as a hydrogenating catalyst, yielding hydrogen sulphide, whilst, on the other hand, the sulphur behaves as an oxidising catalyst, since it ultimately forms water from the free oxygen and the hydrogen of the food. Whereas the sulphur of the food is incapable of reacting with philothionic hydrogen and is thus



without influence, that supplied in the sulphur water increases the oxidation of the hydrogen in the foodstuffs. H. W.

**Preparation of Arseno-metallic Derivatives.** FARBERGER VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270258. Compare this vol., i, 345, 761).—In the preparation of these compounds, the use of ready-formed arseno-compounds may be avoided, as they may be formed by reduction of the corresponding substituted arsenic acids or oxides in presence of metallic salts. T. H. P.

**Preparation of Methylglycylphenylarsinic Acid and its Reduction Product, Bismethylglycylarsenobenzene.** LES ÉTABLISSEMENTS POULENC FRÈRES and KARL OESCHLIN (Fr. Patent, 462276).—*Methylglycylphenylarsinic acid*,  $\text{AsO}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained by hydrolysis of its esters by means of excess of sodium hydroxide at about  $60^\circ$  and subsequent acidification, forms small, white crystals, and when heated does not melt, but yields carbon dioxide and dimethylaminophenylarsinic acid, which decomposes at  $280\text{--}300^\circ$ . On reduction by means of sodium hyposulphite at a high temperature, it is converted into *bismethylglycylarsenobenzene*,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{As} \cdot \text{As} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . T. H. P.

**Preparation of Additive Metallic Derivatives of Arseno-phosphorus and Arseno-antimony Compounds.** FARBERGER VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 270259).—Additive compounds of metallic salts with organic arseno-phosphorus and arseno-antimony compounds may be obtained by methods similar to those described earlier (this vol., i, 345, 761). They are very similar to the arseno-metallic derivatives and are of therapeutic value. T. H. P.

## Physiological Chemistry.

**The Basal Gaseous Metabolism of Normal Men and Women.** FRANÇOIS G. BENEDICT, LOUIS E. EMMES, PAUL ROTH, and H. MONMOUTH SMITH (*J. Biol. Chem.*, 1914, 18, 139—155).—The authors record the respiratory exchanges of a large number of healthy persons, male and female, with the corresponding temperature and pulse rate. The observations were usually made for periods of fifteen minutes, the average of several periods, taken on the same or different days, being recorded. A discussion of the results is not appended.

H. W. B.

**The Sensitiveness of Oxygen Respiration [of the Cell Granule] towards Indifferent Narcotics.** OTTO WARBURG (*Pflüger's Archiv*, 1914, 158, 19—28).—The respiratory function of the granules contained in a centrifugised extract of liver with

dilute potassium chloride solution is depressed 50% by the following concentrations of narcotics expressed in milli-mols. per litre: methyl carbamate, 960; urethane, 360; propyl carbamate, 150; isobutyl carbamate, 33; isoamyl carbamate, 14. On the other hand, the aqueous extract of liver, containing material dissolved out of the granules, has less respiratory power than the suspension of granules, and considerably greater concentrations of the narcotics must be employed to bring about a 50% depression of respiratory power, namely, methyl carbamate 2000 milli-mols. per litre, urethane 740, propyl carbamate 500, isobutyl carbamate 90, isoamyl carbamate 40. The granules, therefore, are not enzymes, but organised structures (organisms).

H. W. B.

#### Elimination of Carbon Dioxide during Manual Labour.

GÖSTA BECKER and J. W. HÄMÄLÄINEN (*Chem. Zentr.*, 1914, i, 1359; from *Skand. Archiv. Physiol.*, 31, 198—240).—The elimination of carbon has been determined for a series of manual workers who were employed at their respective occupations in a large breathing chamber for three experiments, each lasting two hours. Experiments were performed on two workers for each occupation, and a remarkable similarity was found in the elimination of carbon by different persons similarly employed. The varying demands of different occupations on the bodily strength of the workers are well marked by the figures obtained for the carbon elimination. They are least, for example, for cobblers and tailors, greatest for masons and sawyers. The average of the carbon elimination (in grams) in the middle of the working period is 15·63 or 15·56 for cobblers, 11·27 or 12·31 for tailors, 37·07 or 33·28 for masons, and 45·50 or 40·96 for wood sawyers. Of female workers, sempstresses (7·5 or 8·0) are at one end of the scale, washerwomen (25·91 or 16·91) at the other end.

H. W.

**The Intake of Methyl Alcohol in Inspiration.** A. LÖWY and R. VON DER HEIDE (*Biochem. Zeitsch.*, 1914, 65, 230—252).—Rabbits and dogs were exposed in a respiration chamber to air containing various quantities of methyl alcohol vapour. These amounts could be regulated by passing air through methyl alcohol in various dilutions in water. The air was measured by a meter, and the amount of alcohol was estimated at the beginning and end of the experiment. The toxic effects were noticed, and the alcohol in the animal bodies was estimated at the end of the experiment. In the presence of only 0·2% of alcohol in the air, quite appreciable quantities were taken up by the organism. With alcohol of this tension, and up to 0·5%, the saturation of the animal body is reached in two hours. With higher concentrations, the times required for saturation are markedly longer, and when the tension reached 2½% the maximal amount is not taken up even after eight hours. Fat animals, under similar conditions, take up less alcohol than lean ones. This is due to the small solubility in lipoids of methyl alcohol; the coefficient of distribution between oil and water is about 2½ : 100.

S. B. S.

**The Absorption and Dissociation of Carbon Dioxide by the Human Blood.** JOHANNE CHRISTIANSEN, C. G. DOUGLAS, and J. S. HALDANE (*J. Physiol.*, 1914, 48, 244—271).—Under normal conditions, the curve representing the relation between the amount of carbon dioxide taken up by fresh, defibrinated blood and the pressure of the gas is a very definite constant for the same individual, and does not vary very much for different individuals. At 40 mm. pressure, 100 volumes of oxygenated human blood take up about 50 volumes of gas, and at 80 mm. about 15 volumes more. Blood which has been deprived of oxygen takes up more carbon dioxide than oxygenated blood under the same pressure. Oxygen tends, therefore, to drive out the carbon dioxide, and the action depends on the saturation of the haemoglobin. A curve is given showing the extent of this action with varying pressures of carbon dioxide. By means of these facts, an explanation is offered as to the method by which carbon dioxide is driven out of the lungs by oxygenation. With the help of these and other data, it is also shown how it is possible to calculate the carbon dioxide pressure of the venous blood reaching the lungs, and the rate of blood flow through these organs.

S. B. S.

**The Rate of Disappearance of Ammonia from the Blood in Normal and in Thyroidectomised Animals.** CLARA JACOBSON (*J. Biol. Chem.*, 1914, 18, 133—137. Compare A., 1910, ii, 324; 1911, ii, 632).—The author has determined the rate of disappearance of ammonia from the circulating blood after intravenous injections of ammonium carbonate, the renal vessels being ligatured to prevent escape through the kidney. The ammonia was estimated by a modification of Polin's method, the normal quantity present in cat's blood being 0.6 mg. per kilo. body-weight.

So rapidly does ammonia disappear from the blood, that five minutes after the injection of ammonium carbonate equivalent to 100 mg. of ammonia per 100 c.c. of blood, the ammonia content of the blood is scarcely above normal. No perceptible difference is observed in the case of parathyroidectomised animals, and even when the liver is also excluded the ammonia content of the blood five minutes after the injection is not more than 8 mg. per 100 c.c. of blood.

H. W. B.

**The Distribution of Glycogen in the Blood During Resorption of Carbohydrates from the Small Intestine.** OSW. POLIMANTI (*Biochem. Zeitsch.*, 1914, 64, 490—494).—A dog was killed during the height of digestion after a diet rich in carbohydrates, and the amount of glycogen in various parts of the circulation was determined. The following quantities were found in 100 grams of blood: in the carotid artery, 58.21 mg.; in the *vena cava abdominalis*, 34.25; and in the portal vein, 96.75. The author expresses the opinion that the synthesis of glycogen takes place in the intestinal wall.

S. B. S.

The Fermentative Properties of the Blood. IV. The Proteoclastic Properties of the Formal Elements of the Blood. LUDWIG PINCUSOHN and KURT RÜDIGER VON ROQUES (*Biochem. Zeitsch.*, 1914, 64, 1—12. Compare A., 1913, i, 788, 1404; this vol., i, 895).—The proteoclastic action of the blood corpuscles (intact and lysed) from various species on different organs was investigated, the Abderhalden dialysis method being employed. It was found invariably that no proteoclastic action could be detected when ninhydrin was used as the reagent. S. B. S.

The Esterase of Blood. VI. Comparative Experiments with the Lipase of the Pancreas and the Esterase of the Blood. P. ROMA and Z. BIEN (*Biochem. Zeitsch.*, 1914, 64, 13—29. Compare this vol., i, 341).—The optimal activity of the pancreatic lipase lies between  $p=8.3$  and 9, a region distinctly more alkaline than that found for blood lipase. The anions are the active portion. The acid dissociation constant is  $1.8 \times 10^{-7}$ , as compared with  $1 \times 10^{-6}$  for the blood-lipase. The two lipases are not therefore identical. The action of the pancreatic lipase is accelerated by calcium, barium, magnesium, and manganese salts, which are without action on the blood lipase. Sodium fluoride inhibits the blood-lipase action to a much larger extent than it does that of the pancreatic lipase. The latter appears to act in a heterogeneous, the former in a homogeneous, system. S. B. S.

Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation. IV. Formation of Gels in Liquid Plasma and Transudates obtained by the Action of Acids; the Reversibility of these Gels and the Properties of their Sols. The Significance of Alkalescence as a Factor in Delaying or Checking Coagulation. E. HEKMA (*Biochem. Zeitsch.*, 1914, 64, 86—102. Compare this vol., i, 754, 895).—Gel formation in natural fluids containing fibrinogen (transudates, etc.) can be slowed or inhibited by the addition of alkalis, but can be caused to take place, on the other hand, by the addition of acids or acid salts, until the liquid is near the neutral point. Such natural fluids behave towards acids and alkalis in the same way as the artificially prepared alkaline hydrosol of fibrin. The gels produced from such preparations, and those prepared from natural liquids by acids, are quite similar in their properties. The gels produced by "spontaneous" clotting of natural fluids and by serum from natural fluids and alkali hydrosols are also similar. All the gels produced by various methods are reversible. It is presumed that gel-formation is in all cases due to the same protein. S. B. S.

Fibrin in its Relation to Problems of Biology and Colloidal Chemistry. The Problem of Blood Coagulation. V. E. HEKMA (*Biochem. Zeitsch.*, 1914, 65, 311—331. Compare this vol., i, 754, 895, and preceding abstract).—The author supplements his previous work with certain experiments on the influence of salts on gel-formation from plasma and transudates. S. B. S.

**The Physico-chemical Mechanism of Hæmolysis by Specific Hæmolysins. II. The Electrical Conductivity of Sensitised Corpuscles and the Action of Inorganic Ferments or Metal-sols on them.** UPENDRA NATH BRAHMACHARI (*Biochem. J.*, 1914, 8, 227—229. Compare this vol., i, 347).—The adsorption of amboceptor by erythrocytes is followed by a diminution in the electrical conductivity of the corpuscles, due to the combination of the amboceptor with the corpuscular wall.

Metal sols, as well as other catalysts, such as animal charcoal, platinum black, and colloidal iodine, do not bring about any hæmolysis of sensitised corpuscles. H. W. B.

**Influence of a Number of Foods on the Secretion of the Digestive Glands.** OSKAR WOLFSBERG (*Zeitsch. physiol. Chem.*, 1914, 91, 344—371).—Meat, meat extract, and milk cause an increase in secretion in the proportion to the quantity of food introduced, whilst potato, butter, bread, and probably sugar do not. The increased secretion is due to "extractives," which activate the hormone of the pyloric mucous membrane. The amount of secretion caused by a given stimulus in given circumstances is approximately constant. When the amount of secretion is doubled, the time required to empty the stomach is not doubled; it is often hardly increased. R. V. S.

**The Dynamic Side of Biochemistry.** F. GOWLAND HOPKINS (*Rep. Brit. Assoc.*, 1913, 652—668).—Presidential address to Section I (Physiology). Metabolism deals mainly with simple molecules, and a very large part of the chemical dynamics of the cell consists of simple reactions catalysed by independent specific enzymes.

C. H. D.

**The Relationships of Lactic Acid to Carbohydrate Metabolism. I. The Appearance of Lactic Acid in the Urine of Rabbit in Phosphorus Poisoning.** OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1914, 64, 131—155).—No increase in the lactic acid was observed in the urine of rabbits which had been fed on greens when doses of 0.005 to 0.20 gram of phosphorus were administered. On the other hand, such an increase took place when much sugar was administered, either immediately after poisoning or in the terminal stages of the toxic action. The increase, however, was small compared with the amount of sugar ingested, and this fact gives the impression that the acid is not a direct product of sugar metabolism, but is perhaps derived from a "lactacidogen." There was no relationship between the amount of lactic acid in the urine and the alimentary glycosuria. Glycer-aldehyde ingestion caused no increase in lactic acid, and dextrose-phosphates caused only such an increase as could be due to the combined sugar. S. B. S.

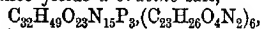
**The Relationships of Lactic Acid to Carbohydrate Metabolism. II. The Lactic Acid Secretion in the Urine of Rabbits which have been Submitted to Low Temperature.** OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1914, 64, 156—171).—Rabbits

in which the body-temperature has been reduced to 30° by immersion in a cold bath excrete lactic acid in the urine. This phenomenon will happen several times with the same animal, provided only that a sufficient interval has elapsed between the intervals of cooling. It seems, therefore, that the animal does not possess an unlimited supply of material yielding lactic acid (lactacidogen). If the animal is submitted to the cooling process when on a diet rich in sugar, it tends readily to excrete the acid, but if the same animal is cooled when in a condition of starvation, after adrenalin injection (so that the body is deficient in carbohydrates), then the increased excretion of lactic acid will disappear. The excretion of lactic acid appears to depend in some way, therefore, on the condition of the supply of carbohydrate in the animal. In one experiment the administration of excess of sugar, without cooling, produced an increased secretion of lactic acid.

S. B. S.

**The Influence of a Vitamine-free Diet on the Carbohydrate Metabolism.** CASIMIR FUNK and COUNT ERWIN VON SCHÖNBORN (*J. Physiol.*, 1914, 48, 328—331).—Pigeons kept on a vitamine-free diet develop hyperglycæmia, with a diminution of the glycogen of the liver. The hyperglycæmia is especially marked in a sugar-free diet, which is followed by the disappearance of the liver glycogen. The addition of vitamine from yeast to such a diet produced in three cases a marked diminution of sugar in the blood and a formation of glycogen in the liver. Vitamine appears, therefore, to affect the carbohydrate metabolism. In the case of the fat-free diet, the glycogen of the liver is increased. S. B. S.

**Nuclein Metabolism. I. Digestion of Yeast Nucleic Acid by Human Duodenal Juice. Isolation of Triphosphonucleic Acid.** S. J. THANNHAUSER (*Zeitsch. physiol. Chem.*, 1914, 91, 329—335).—The product of this digestion (prolonged for seventy-two hours under toluene) does not contain nucleosides or free purine bases, but free phosphoric acid is present. From the mixture a substance, termed *triphosphonucleic acid*, can be isolated. It has the composition  $C_{32}H_{49}O_{23}N_{15}P_3$ ,  $[\alpha]_D^{17} - 19.6^\circ$ . The rotatory power and the titratable acidity of different preparations is the same. The substance yields a *brucine* salt,



which crystallises in prisms, m. p. 200—205°. When hydrolysed with ammonia in an autoclave, triphosphonucleic acid yields guanosine, adenosine, and cytidine.

R. V. S.

**Nuclein Metabolism. II. Metabolism Experiments with Adenosine and Guanosine.** S. J. THANNHAUSER and A. BOMMES (*Zeitsch. physiol. Chem.*, 1914, 91, 336—343).—In rabbits, injection of adenosine or guanosine is followed by an increased excretion of allantoin corresponding with 40% of the substance injected. In healthy men the injection is followed by an increase in the excretion of uric acid (75—82% of the corresponding amount), but no

increase takes place in the uric acid of the blood. In a case of severe gout, no increase in uric acid excretion was observed; in a less severe case a delayed increase in the excretion of uric acid took place. In cases of gout, the amount of uric acid in the blood rises after each injection. In three out of four cases of gout, injection was followed by an attack of gout.

R. V. S.

**Purine Metabolism. I. The Effect of Adrenaline on the Elimination of Allantoin in the Dog.** W. FALTA (*Chem. Zentr.*, 1914, i, 1360; from *Zeitsch. expt. Path. Ther.*, 15, 356—358, Compare Abt, this vol. i, 111).—Experiments show a considerable (about 30%) increase in the elimination of allantoin during the adrenaline periods. Elimination of uric acid is slightly increased.

H. W.

**The Nutrition of Mice on Diets containing Simple Food-stuffs.** F. RÖHMANN (*Biochem. Zeitsch.*, 1914, 64, 30—62).—An account is given of a long series of experiments on diets containing a mixture of pure proteins (caseinogen, egg-albumin, edestin) with starch, fat, and salts. It was found that whereas several such diets were sufficient for the maintenance of adult animals, they were unsuitable for young individuals, in which often, after a short period of development, growth ceased. Certain additions to the diet, such as malt extract and yeast, greatly increased the efficiency, even when administered to young animals. It is claimed that by the last experiments (carried out in 1902) it was demonstrated for the first time that it was possible to rear animals on an artificial diet compounded of simple food-stuffs. A long series of experiments on the value of different proteins is also described; too many factors are, however, involved for any definite conclusions to be drawn. Proteins containing phosphorus (nucleo-proteins) and lecithin were not found to be indispensable. The author discusses the results obtained by Osborne and Mendel in a similar series of experiments, and puts forward a claim for priority.

S. B. S.

**Experiments with Diets which are Qualitatively Insufficient.** S. OSERI (*Biochem. Zeitsch.*, 1914, 65, 158—176).—Rye bread prepared with water is a far more efficient diet for mice than bread prepared from fine wheat flour. The addition, however, of milk, pressed yeast, cruder rye and wheat flours, and the extracts of the same can increase the nutritive value of the fine wheat bread, and even make it equivalent to that of the rye bread. The accessory food substances contained in the rye bread can be readily extracted with water, but not with alcohol and ether, and are apparently, therefore, not identical with the food adjuvants which have been obtained from milk.

S. B. S.

**Suitability of Hardened Fats for Use as Human Foods.** K. B. LEHMANN (*Chem. Zeit.*, 1914, 38, 798—799).—Hardened fats prepared from earthenut, cottonseed and sesame oils were found to

contain from 0.1 to 6 mg. of nickel per kilo. of fat, quantities which are considerably less than those found occasionally in foods prepared in nickel utensils; this slight metallic contamination is not injurious to health, and the author is of opinion that hardened fats may be used as substitutes for the ordinary edible fats, this conclusion being confirmed by the fact that feeding experiments with hardened fats yielded satisfactory results.

W. P. S.

**The Chemical Determinants of Growth.** CASIMIR FUNK and ARCHIBALD BRUCE MACALLUM (*Zeitsch. physiol. Chem.*, 1914, 92, 13—20. Compare Osborne and Mendel, A., 1913, i, 1128).—The authors were unable to maintain rats for more than forty-seven days on an artificial diet of purified casein, starch, sugar, lard and salts, together with butter. The conclusion drawn is that the "protein-free" milk used by Osborne and Mendel in their experiments must contain the growth vitamine, since the rats fed by these experimenters on a similar diet plus "protein-free" milk were maintained practically as long as rats fed on ordinary food.

The authors also describe the effect of feeding chickens with polished rice with and without the addition of cod-liver oil. Without the addition, the chickens die of polyneuritis within two months. The addition of the cod-liver oil prevents polyneuritis, but does not promote growth, showing the presence of anti-polyneuritic vitamine and absence of growth vitamine respectively. The seven months' old chicken has not increased in weight during the last five months, and possesses no secondary sexual characters. A striking photograph showing the relative sizes of chickens fed on polished rice and cod-liver oil, and on a normal diet, is appended.

H. W. B.

**The Movements of the Intestinal Villi.** B. F. HAMBLETON (*Amer. J. Physiol.*, 1914, 34, 446—447).—Microscopical observations have been made by the author on the movements of the intestinal villi when treated with various solutions. Peptone, dextrose, weak alkali carbonates, etc., call forth (1) lashing movements, and (2) alternating shortening and lengthening of the villi. Dilute hydrochloric acid checks the movements, and the villi return to the resting condition and become covered with mucus. Alcohol of 10% strength first stimulates, then depresses, and soon stops the movements entirely. The addition of water or salt solution restores activity again. The behaviour to various drugs has also been investigated.

H. W. B.

**The Action of Univalent Alcohols on the Surviving Intestine of the Rabbit.** YAS KUNO (*Arch. expt. Path. Pharm.*, 1914, 77, 206—217).—Portions of the rabbit's intestine have been suspended in isotonic Tyrode solution to which increasing quantities of methyl, ethyl, propyl, butyl and amyl alcohols have been added, and the effect on the intestinal movements graphically recorded. The chief effect is an inhibitory one, which becomes more pronounced as one passes from methyl up to the amyl alcohol.



With very small doses, the movements may first become slightly greater, but this effect soon passes off, and is replaced by inhibition. The action of the alcohols alters the extent of the movements of the tissue, the actual frequency remaining unchanged.

H. W. B.

**Carbon Dioxide Production from the Nerve Fibre in an Atmosphere of Hydrogen.** SHIRO TASHIRO and H. S. ADAMS (*Amer. J. Physiol.*, 34, 405—413. Compare A., 1913, i, 313; ii, 725).—The author has measured by his new method (*loc. cit.*) the amounts of carbon dioxide evolved from the claw nerve of the spider crab when placed in air and in an oxygen-free atmosphere. In the absence of oxygen, the claw nerve gives off decidedly less carbon dioxide than in air, and the application of a weak induction current which, in air, stimulates the nerve and more than doubles its carbon dioxide output, fails, in the oxygen-free atmosphere, to bring about any acceleration in the production of this gas. These results indicate that oxygen is primarily concerned in nerve metabolism, and are in harmony with the view that the real basis of all protoplasmic irritability is a chemical one. H. W. B.

**The Relation between the Electrolyte Concentration of Some Neutral Perfusion Liquids and the Frequency of Beat of the Frog's Heart.** MARY D. WALLER (*Proc. physiol. Soc.*, xlviii—1; *J. Physiol.*, 1914, 48).—The replacement of part of Ringer's solution by a neutral isotonic solution of a non-electrolyte (carbamide or sucrose) in a perfusing fluid produces a definite diminution of the number of heart-beats, depending on the amount of the substitution. S. B. S.

**Carbohydrate Metabolism of the Isolated Heart of Normal and Diabetic Animals.** O. LOEWI and O. WESELKO (*Pflüger's Archiv*, 1914, 158, 155—188).—Glycogen in the rabbit's heart is not used up on perfusion with Locke's fluid, but it almost completely disappears if the dextrose is omitted from the perfusion fluid. Substitution of levulose for the dextrose, as well as other alterations in the composition of Locke's fluid, also lead to glycogenolysis. Similar results are obtained with hearts from rabbits previously injected with adrenaline (adrenaline-hearts).

Perfusion of normal and adrenaline-hearts from ill-nourished rabbits with Locke's fluid shows that the latter have to some extent lost their power of decomposing the dextrose. Reduction of the amount of potassium or calcium in the Locke's fluid increases the glycolytic action of the adrenaline-heart, a similar effect not being observed with the normal heart. If the perfusion fluid, containing 0.02% of potassium chloride, after leaving the heart, is shaken with oxygen or nitrogen at 38°, the dextrose disappears. This is due to the presence of formed elements from the heart, for, by centrifugalising, the perfusion fluid may be clarified, and has then no glycolytic power. H. W. B.

Degradation of Cholesterol in Animal Organs. VI. Cholesterol. Bile Acids. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1914, 91, 309—328. Compare A., 1913, i, 932).—The unsaponifiable portion of the fat of the liver consists partly of cholesterol and partly of the so-called "non-cholesterols." The latter are cholesterol derivatives, however, for on oxidation, the acetic acid-sulphuric acid reaction of oxycholesterol can be obtained. This reaction is also given (after oxidation) by the bile acids and by the bile itself.

R. V. S.

Mobilisation of Sugar in the Surviving Liver of the Cold-blooded Animal. A. FRÖHLICH and L. POLLAK (*Arch. exp. Path. Pharm.*, 1914, 77, 265—298).—The authors have endeavoured to ascertain whether the glycosuria resulting from the administration of various substances to the cold-blooded animal is due to a direct action on the liver cell, leading to the formation of sugar from stored glycogen, or is an indirect one operating through the nervous system.

Direct perfusion of the surviving liver of the frog with adrenaline leads to glycogenolysis, but this is prevented if ergotoxin, which paralyzes sympathetic nerve endings, is simultaneously present in the perfusion fluid. On the other hand, ergotoxin does not inhibit the glycogenolysis brought about by ether or pituitary extract, which, therefore, has a different point of attack in the liver, leading, however, to the same end-result.

The formation of dextrose following perfusion with pyruvic and other ketonic acids is due, not to their being transformed into dextrose, but to their stimulating action on glycogenolysis, because the effect is immediate, even at the low temperature and depressed metabolic activity associated with the tissues of the cold-blooded animal. Moreover, other ketonic acids, such as benzoylactic acid, from which dextrose could not readily be produced, bring about the same effect, and, further, their action is annulled if ergotoxin is also added to the perfusing solution exactly as is the action of adrenaline.

As to the cause of the increased glycogenolysis, it may be due to an easier passage of the diastase to the glycogen in the cell or to the new formation of, or activation of, preformed enzyme. Perfusion with a diastase solution does not hasten the change; neither does the addition of adrenaline hasten glycogenolysis in minced liver; but ether does. The conclusion so far is that different agents act in different ways.

H. W. B.

The Importance of the Liver in the Formation of Urea from Amino-acids. CYRUS H. FISKE and JAMES B. SUMNER (*J. Biol. Chem.*, 1914, 18, 285—295).—Experimental evidence is brought forward showing that the liver is not the only site of the formation of urea in the animal organism.

The influence of the liver, kidney, and other abdominal organs on the blood circulation in the cat has been removed by the ligation of the corresponding arteries and veins, and it has then

been found that the injection of solutions of amino-acids is followed by the formation of urea, just as when the liver is present. The increase in urea was observed in both blood and muscles, and was of about the same extent in "operated" as in "control" animals.

H. W. B.

**The Ferments of the Pancreas. IV. Steapsin.** JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1914, 48, 287—302).—

The stability of steapsin in alkaline solution is similar to that of trypsin. Fresh pancreatic juice loses 10% in an hour at 40°, 50% at 50°, and at 60° the whole is destroyed within five minutes. Steapsin is stable in the presence of large quantities of the higher fatty acids, but is rapidly destroyed by minute amounts (0.02% hydrochloric acid) of free mineral acids. It cannot exist in the presence of free trypsin, and is therefore rapidly destroyed when pancreatic juice is activated by enterokinase. Serum or egg-albumin protect the steapsin from destruction under these conditions, owing to their containing antitrypsin. The lipolytic activity is largely increased by bile and bile salts, but electrolytes have little influence. There is no evidence that pancreatic steapsin can be separated into an enzyme and co-enzyme. The destruction of steapsin by trypsin is absolute, and the ferment cannot be reactivated by the addition of serum or bile.

S. B. S.

**Physiology of the Thyroid. IV. Fate of Iodine in the Thyroid Gland.** F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, 91, 400—424. Compare this vol., ii, 670).—Most of the iodine of the thyroid gland is present in the form of a compound with protein, but a small portion exists in the form of compounds soluble in acetone; among these the presence of free alkali iodide can be demonstrated. Alkali iodide occurs in this way, even when it cannot have been contained in the food. The quantity of iodine found in the thyroid gland varies greatly; in the sheep 1—1.5 milligrams per gland is an average value; in the dog the quantity is less on the average, but varies more. When alkali iodide is administered, the amount of iodine in the thyroid increases, but it is present there in organic combination. The iodo-protein of the thyroid (thyreoglobulin) has not a constant iodine percentage; the percentage increases after administration of alkali iodide. Administration of alkali iodide after removal of one lobe of the gland causes an increase in the amount and iodine percentage of the thyreoglobulin in the remaining lobe. When iodine is no longer present in the food, it remains in the thyroid, and if it was present there in unusual amount before, the amount remains high afterwards.

R. V. S.

**Physiology of the Thyroid. V. Does Iodine Occur in Blood?** F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, 91, 450—464).—Iodine found in the blood can be considered of thyroid origin only if it is in organic combination, and this the authors have been unable to find in normal blood. Iodine in inorganic

combination when present in the blood has arisen from the food, and is a transient occurrence. Animals fed with iodine-free food have no inorganic iodine in their blood, although their thyroids contain much iodine.

After administration of alkali iodide "inorganic" iodine can be detected in the blood for a long time. In some pathological conditions (eclampsia, nephritis) "organic" iodine probably of thyroid origin can be found in some of the cases.

R. V. S.

**The Significance of the Thyroid Gland in Carbohydrate Metabolism.** GUNNAR BÖR (*Biochem. Zeitsch.*, 1914, 64, 450—470).

—The experiments were carried out on rabbits, and the estimations of blood-sugar were made by Bang's microchemical method. The values of the blood-sugar are not altered either by hypo- or hyperthyroidism. The administration of thyroid gland does not alter the action of adrenaline on the blood-sugar. On the other hand, it inhibits the action of pituitrin on adrenaline hyperglycemia. In hyperthyroidism the inhibitory action of pituitrin on the thyroid is weakened, whereas in athyroidism it is increased. Some months after thyroidectomy, an increase in the weight of the pituitary body can be observed; in the course of this time the diminished action of the thyroids on the pituitary body is compensated; anatomical investigations show that the compensation takes place contemporaneously with a hypertrophy of the glandular portion of the pituitary body; this organ appears, therefore, to act as a reserve to the thyroid action on the blood-sugar.

S. B. S.

**The Active Principle of the Pituitary Body.** M. GUGGENHEIM (*Biochem. Zeitsch.*, 1914, 65, 189—218).—In addition to the ordinary proteinogenous amines which occur in other organs, the pituitary body contains a specific substance, which can be distinguished by its characteristic actions on blood pressure and respiration, but, above all, by its production of increased tone in the rat's uterus. The substance in question is extremely sensitive to the action of alkali hydroxides, which destroy it, and is in this respect analogous to pilocarpine, to which it is also alike in certain pharmacological actions. The activity of the pituitary substance differs from this alkaloid in that its activity cannot be restored after it has once been destroyed by alkalis. It is, however, more nearly allied, both chemically and pharmacologically, to acetylcholine. It differs from this base in that the latter, after repeated injection into the same animal, still reproduces the same effects, whereas the animal fails to react to the rise in blood pressure after repeated doses of the pituitary substance. The author believes that the active substance is an ester-like derivative of an alkanolamine with an acetyl residue.

S. B. S.

**Chemistry of Lipoid Substances in the Suprarenal Capsules.** H. BRUMER (*Arch. expt. Path. Pharm.*, 1914, 77, 304—316). Several phosphatides have been extracted from the suprarenal glands of the sheep and ox, including two monoaminomonophospha-

tides, lecithin and cephalin, cuorin, sphingomyelin, jecorin, and two other phosphatides. Cholesterol was also found in the suprarenals of both animals, chiefly in the free state, with only a small proportion in the form of ester.

No relation could be established between the content of cholesterol ester in the blood serum and suprarenals respectively. The suprarenals have the power of storing up cholesterol esters and free fatty acids.

H. W. B.

**The Cephalin and Other Lipoids of the Cortex of the Suprarenals.** RICHARD WAGNER (*Biochem. Zeitsch.*, 1914, 64, 72—81).—The following lipid substances could be found in the cold alcoholic extract of suprarenals—a monoaminophosphatide (cephalin), which is insoluble in acetone and absolute alcohol, but soluble in ether; a substance insoluble in acetone, alcohol, or ether, but soluble in chloroform or benzene, which darkens in the air and contains nitrogen and phosphorus (corresponding with the sphingomyelin of other authors); a phosphatide of the character of lecithin, which is insoluble in acetone, but soluble in alcohol or ether, and various nitrogen-free fats. A substance of aminolipoid character was not obtained. The cephalin yields on hydrolysis a substance which is probably hydroxyethylamine.

S. B. S.

**The Amount of Carnosine in Mammalian Muscle.** OTTO VON FÜRTH and THEODOR HRYNTSCHAK (*Biochem. Zeitsch.*, 1914, 64, 172—193).—The so-called carnosine fraction of meat extract (that is, the part precipitated by silver salts and barium hydroxide after preliminary separation of the colloids by lead acetate) contains some nitrogenous substance other than carnosine. The true carnosine content in this fraction can, however, be estimated by two colorimetric methods. One of these depends on the colour yielded by the histidine complex in the molecule with diazobenzenesulphonic acid, and the other on the violet colour yielded by carnosine itself when boiled with cupric hydroxide. It is possible to obtain the copper salt, to which this colour is due, in a crystalline form, but, as a rule, not more than one-half to two-thirds of the carnosine present can be so isolated. The amount of carnosine in 1 kilo. of meat is estimated to be between 2 and 3 grams.

S. B. S.

**The Amino-acids of Horse-flesh Hydrolysed by Sulphuric Acid.** TULLIO GAYDA (*Biochem. Zeitsch.*, 1914, 64, 438—449).—Analyses of the distribution of nitrogen in the products of hydrolysis by van Slyke's method have been carried out. The comparison of the numbers obtained by other authors for other varieties of muscular tissue is made, and the evidence indicates that these proteins have different constitutions.

S. B. S.

**The Influence of Ultra-violet Rays on the Colour of the Hair of Rabbits and Guinea-pigs.** S. SÉCEROV (*Compt. rend.*, 1914, 158, 1826—1828).—Exposure of white-haired guinea-pigs or rabbits to the action of ultraviolet rays at a distance of 9—10 cm.

from the lamp for a considerable time produces a coloration of the hair. In the case of the guinea-pig the white hairs become yellow after thirty-five to forty hours, and in the case of the rabbit after eighty hours, the colour finally becoming reddish-yellow. The coloration only occurs at those parts directly exposed to the rays. In the case of animals partly black- and white-haired the coloration of the white hairs takes place more rapidly than with a pure white animal. The coloration is produced in the hair when detached from the animal, but less rapidly than when growing. Heat produces a yellow coloration, but a temperature of  $150^{\circ}$  is necessary.

W. G.

**The Purine Enzymes of the Orang-utan (*Simia Satyrus*) and Chimpanzee (*Anthropopithecus Troglodytes*).** H. GIDRON WELLS and GEORGE T. CALDWELL (*J. Biol. Chem.*, 1914, 18, 157—165).—No enzymes capable of decomposing uric acid were found by the authors in the tissues of an orang-utan and of a chimpanzee. These results are in accord with Wiechowski's observation that the chimpanzee excretes uric acid and no allantoin in the urine. The anthropoid apes resemble man, therefore, in this respect, wherein they constitute a marked exception to all other mammals, including the monkey. The anthropoids, like adult man, also contain little, if any, adenase, but guanase is present in nearly all their tissues. Xanthine-oxydase was present in the liver of the chimpanzee, but not in any tissues of the orang-utan.

H. W. B.

**Some Extractives from the Crayfish. Formation of Creatine in Animals.** FR. KUTSCHER (*Zeitsch. Biol.*, 1914, 64, 240—246).—The muscle of the crayfish (*Astacus fluviatilis*) contains the same extractives as that of the shrimp (compare Ackermann and Kutscher, A., 1907, ii, 283, 491; 1908, ii, 53), namely, leucine, tyrosine, purine bases, *D*-arginine, betaine, and neosine. The presence of arginine instead of creatine in these cold-blooded animals, with depressed oxidative processes, confirms the view that arginine is the precursor of creatine in muscle.

H. W. B.

**The Secretions of Fishes' Skins. Part I. The Chemistry of Eel-slime.** JOHANNES MÜLLER and HANS REINBACH (*Zeitsch. physiol. Chem.*, 1914, 92, 56—74).—Eel-slime contains about 12% dry substance, 75% of which consists of a protein resembling the nucleo-albumin of snail's liver. The remainder is made up chiefly of lipoids, namely, esters of cholesterol, a crystalline diaminomonophosphate,  $C_{41}H_{106}O_{15}N_6P$ , which commences to liquefy at  $120^{\circ}$  and melts finally at  $177$ — $179^{\circ}$ ; a diaminomonophosphate,  $C_{39}H_{102}O_{14}N_6P$ , which is possibly an oxidation product of the crystalline phosphatide; a phosphatide of the lecithin type; and a basic substance of betaine nature. No true mucin was detected.

H. W. B.

**Reactions of Earth-worms to Hydroxyl Ions.** A. T. SHONL (*Amer. J. Physiol.*, 1914, 34, 384—404).—The author has placed

earthworms (*Allolobophora foetida*) in contact with alkali solutions of various concentrations, and has measured the times which have elapsed before the worms have withdrawn themselves from the solutions (reaction time). The reaction time has been found to be proportional to the number of hydroxyl ions in the solution, and to be independent of the anion. Temperature is an important factor; the higher the temperature the quicker the reaction.

H. W. B.

**Estimation and Significance of the Ammonia Content of Milk.** J. TILLMANN, A. SPLITZGERBER, and H. RIFFART (*Zeitsch. Natur. Genusss.*, 1914, 27, 801).—In connexion with their recent paper on this subject (this vol., i, 454), the authors wish to make mention of a previous investigation by Rullmann (A., 1911, ii, 667). The latter found larger quantities of ammonia in fresh milk than did the authors in their experiments, the difference probably being due to the fact that Rullmann distilled the milk with the addition of calcium hydroxide.

W. P. S.

**Source of the Thiosulphate in Rabbit's Urine.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1914, 92, 89—103).—The substance which causes the appearance of thiosulphate in rabbit's urine is contained in an aqueous extract of cabbage. It is not thiosulphate, but is destroyed by warming with hydrochloric acid. The administration of thiosulphate, sodium sulphite, and sodium sulphate is, in each case, followed by the elimination of a small amount of thiosulphate in the urine.

White cabbage contains about five times as much organic sulphur as carrots, and after feeding rabbits with these materials the urine contains corresponding quantities of organic sulphur. H. W. B.

**Alteration in the Oxidation of Methyl Alcohol by Other Alcohols.** ERNST ASSER (*Chem. Zentr.*, 1914, i, 1359; from *Zeitsch. expt. Path. Ther.*, 15, 322—334).—It has been shown by Król (*Arch. expt. Path. Pharm.*, 1913, 72, 444) that formic acid is an intermediate product in the oxidation of methyl alcohol. Determinations of formic acid in the urine (compare Fincke, A., 1913, ii, 636) show a decrease in the amount of acid after administration of alcohol, amyl alcohol, or acetone. If this effect is due to a limitation of the oxidation, an increase in the amount of exhaled methyl alcohol might be expected; an experimental investigation by the method of Völtz and Dietrich (A., 1912, ii, 575) shows that this is not the case. The diminished elimination of formic acid must therefore be attributed to an increased oxidation of the latter. If these results, obtained with formate and ethyl alcohol, are applied to experiments with methyl and ethyl alcohols (in which the former may be regarded as a source of formic acid), the conclusion may be drawn that the administration of ethyl alcohol increases the power of oxidation of formate in the body.

H. W.

**Creatinine and Indican in the Urine of Domestic Animals.** HUGO MÜNZER (*Pflüger's Archiv*, 1914, 158, 41—83).—The amounts

of creatinine and indican in a large number of animal urines have been determined by means of the Autenrieth-Königsberger colorimeter. The average quantities in grams per litre of urine were, as regards creatinine, horse 1.94, pig 1.49, sheep 1.44, ox 1.12, goat 0.38, and indican, horse 0.039, sheep 0.037, ass 0.024, ox 0.020, pig 0.01, goat 0.005. Calves on milk diet passed more creatinine than full-grown animals.

H. W. B.

**The Contribution of Bacteria to the Faeces after Feeding Diets free from Indigestible Components.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1914, 18, 177—182).—The amount of bacteria in the faeces of rats fed on various artificial diets has been determined by extracting the dried faeces successively with ether, alcohol, 80% alcohol, 0.2% hydrochloric acid, and alcohol containing 0.2% hydrochloric acid. The dry residue was assumed to be composed almost entirely of bacteria on the grounds that a stained specimen had the characteristic appearance of bacteria similarly treated, and that it contained about the same percentage of nitrogen (10.7 to 12.2) as most bacterial cellular substances. The actual amount of bacteria thus determined varied from 30 to 40% of the dry faeces.

H. W. B.

**The Bone Disorders Produced by Diet Poor in Phosphorus. III.** M. MASSLOV (*Biochem. Zeitsch.*, 1914, 64, 106—110. Compare A., 1913, i, 1264, 1265).—The author gives a description of the histological appearance of the bones of animals which have been fed on a diet poor in phosphorus. The general characters are somewhat similar to those observed in Barlow's disease.

S. B. S.

**Gluconeogenesis. IX. The Formation of Dextrose from Dihydroxyacetone in the Diabetic Organism.** A. I. RINGER and E. M. FRANKEL (*J. Biol. Chem.*, 1914, 18, 233—236. Compare this vol., i, 903).—The subcutaneous administration of dihydroxyacetone to phloridzinised dogs is followed by a rise in the amount of dextrose eliminated in the urine. In one experiment the dihydroxyacetone appeared to be quantitatively transformed into extrose. The injection of dihydroxyacetone inhibited the acidosis in three out of the four experiments.

H. W. B.

**The Excretion of Creatine in Severe and Mild Cases of Diabetes Mellitus.** R. A. KRAUSE (*Proc. physiol. Soc.*, xliii—xliv; *J. Physiol.*, 1914, 48).—Even in a mild case of diabetes mellitus, with no appreciable amount of acidosis, creatine could be detected in the urine.

S. B. S.

**Creatine and Creatinine Metabolism. III. The Origin of Urinary Creatine.** STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1914, 18, 195—214).—The authors have studied the effects of a creatine-free protein diet on the elimination of creatine and creatinine in dogs completely under the influence of phlorid-



zin. The amount of creatinine in the urine slowly diminishes, no matter whether the animal is in a fasting state or fed on protein. The amount of creatine varies considerably, and is wholly independent of the amount of body tissue destroyed. Analysis of the muscular tissue of the animals at the end of the experimental periods showed the presence of amounts of creatine rather above the normal, so that the creatine eliminated in the urine did not have its origin in preformed creatine of the muscles. The view expressed is that creatine is probably being formed in the animal organism in relatively large amounts, and is normally either utilised or destroyed, the power to metabolise creatine being directly related to that of metabolising carbohydrate.

The relation of urinary creatinine to muscle creatine has not yet been established.

H. W. B.

Gout. III. H. BECHHOLD and J. ZIEGLER (*Biochem. Zeitsch.*, 1914, 64, 471—489).—Measurements of the solubilities of uric acid and sodium urate in water, salt-free sera, normal sera, and sera with and without the globulin fraction, are given. The measurements were made either by cooling supersaturated solutions or by shaking the fluid with excess of solids. In using the first method an important factor must be taken into account, namely, the time, for whereas in the case of aqueous solutions the separation of the excess of solute takes but a short time, a prolonged period elapses in the presence of serum before the solution reaches a constant composition. Attention is called to the importance of this factor in the study of gout. Experiments carried out by the ultra-filtration method tend to show that sodium urate can exist in colloidal solution.

S. B. S.

The Mechanism of Certain Forms of Hyperglycæmia produced Experimentally in Rabbits. II. and III. IVAS BANG (*Biochem. Zeitsch.*, 1914, 65, 283—295, 296—310. Compare this vol., i, 230).—II. The author finds that diuretin in many cases does not lead to hyperglycæmia, and that the results with this drug are by no means uniform. Generally, the combined action of diuretin and larger amounts of urethane leads to hyperglycæmia, but the want of uniformity in the results compels him to abandon the hypothesis he has previously put forward, as to the psychic action of the diuretin, although he believes that small amounts of narcotics can partly or wholly suppress various forms of hyperglycæmia (compare this vol., i, 230). Hyperglycæmia due to the combined administration of urethane and diuretin is due to the former.

III. The author draws the conclusion that hyperglycæmia due to urethane is not a form of adrenaline hyperglycæmia. It is produced with certainty only by relatively large doses of the drug (1·7 grams per kilo. of body weight or over); it is more readily produced in animals in low condition (after treatment previously with the drug, or other drugs which have affected its general condition, or in fasting animals); it is independent of the store of

glycogen in the liver, and it is not inhibited by pituitrin. The author believes that the urethane affects the lipoids of the organs of the body generally, and especially those of the pancreas, and the glycosuria and hyperglycemia produced are analogous in many respects to those in pancreatic diabetes. The hyperglycemia is of about the same intensity in both cases; glycosuria sets in with a relatively low degree of hyperglycemia, and is, furthermore, in both cases accompanied by acetonuria. In the two last instances it differs from adrenaline glycosuria. It is not improbable that glycosuria due to narcotics is the effect of the stoppage of the secretion of the pancreatic hormone.

S. B. S.

**The Excretion of Potassium during Malaria.** ALADÁR ELFER and BÉLA VON PURJESZ (*Biochem. Zeitsch.*, 1914, 64, 63—71).—In malaria infection it was found, in the case of the patient under investigation, that the increased output of nitrogen was accompanied by an increased output of potassium. This potassium loss is still evident when the utilisation of sodium and chlorine is normal. The potassium metabolism is similar in this respect to the nitrogen metabolism, but the deficit in the latter element, in contrast to potassium, is most marked in the period of high temperature.

S. B. S.

**A Case of Pentosuria.** II. P. A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1914, 18, 319—327. Compare A., 1913, i, 1274).—The osazone and *p*-bromophenylhydrazone of the urinary pentose have been prepared and contrasted with similar compounds obtained from *d*- and *l*-xylose, *d*- and *l*-arabinose, and *d*-lyxose, with none of which, however, have they been found to be identical. The osazone has m. p. 160°, with effervescence at 163°, and  $\alpha_D + 0.15^\circ$  (in pyridine alcohol), rising to  $+0.57^\circ$  in eighteen hours. The pentose-*p*-bromophenylhydrazone ( $C_{11}H_{15}O_4N_2Br$ ) has m. p. 130—131° (corr.), and decomposes at 154°. The rotation in alcohol increased from  $[\alpha]_D - 1.00^\circ$  to  $+1.12^\circ$  in eighteen hours. *l*-Xylose-*p*-bromophenylhydrazone had  $[\alpha]_D - 0.06^\circ$  in alcohol, rising to  $+0.06^\circ$  in eighteen hours. *d*-Lyxose-*p*-bromophenylhydrazone had m. p. 161.5° (corr.) and  $[\alpha]_D + 1.06^\circ$  in pyridine, changing to  $+0.26^\circ$  in twenty-four hours. *d*-Lyxose-*p*-nitrophenylhydrazone melted at 172° (corr.).

Hydrolysis of the urinary pentose-*p*-bromophenylhydrazone was carried out with benzaldehyde, but the free sugar was not obtained in crystalline form, nor did it furnish a crystalline oxidation product. The conclusion is drawn that the pentose is a keto-pentose corresponding with *l*-lyxose or *d*-xylose.

H. W. B.

**The Curative Action of Autolysed Yeast against Avian Polyneuritis.** EVELYN ASHLEY COOPER (*Biochem. J.*, 1914, 8, 250—252).—Small doses of autolysed brewer's yeast readily cure avian polyneuritis. The liquid retains its curative properties for at least eight weeks, and, when given to birds in doses ten times as great as the minimum curing dose, has no toxic action. Air-

dried yeast retains its curative power for two years. The use of autolysed yeast as suitable material for the preparation of anti-beriberi vitamine is recommended.

H. W. B.

**Metabolism in Bence-Jones Proteinuria.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 18, 277—283. Compare Hopkins and Savory, A., 1911, ii, 417).—A case of multiple myeloma of the ribs is described, in which a few observations were made of the effect of diet on the excretion of the Bence-Jones protein. For the determination of the amount of Bence-Jones protein, 10 c.c. of the urine and 1 c.c. of 5% acetic acid were heated in a weighed centrifuge tube for some hours at 60°, then centrifuged, and the deposited protein washed with alcohol and dried at 100°. During the first period the patient, on a low protein diet, excreted about 2 grams per day of the Bence-Jones protein, which during the following period, on a high protein diet, increased to 6.5 grams, the total nitrogen also rising from about 6 to 16 grams per day. Much creatine was also eliminated during the latter period. After a short interval the patient fasted for two days, when 5 grams of Bence-Jones protein and 8.4 grams of non-protein nitrogen were daily eliminated. Equal amounts of Bence-Jones protein were excreted during twelve-hour day and night periods.

The conclusions reached are that the formation of the Bence-Jones protein is independent of the total protein metabolism, and is probably due to an internal autolytic digestion.

H. W. B.

**The Occurrence of a Crystallisable, Non-coagulable [Bence-Jones] Protein in the Urine of a Patient with Cancer of the Stomach.** O. SCHUMM and A. KIMMERLE (*Zeitsch. physiol. Chem.*, 1914, 92, 1—13).—A specimen of the urine was treated with sodium chloride and a trace of acetic acid, boiled, and filtered to remove coagulable protein. Alcohol was added to the filtrate, and the resulting precipitate redissolved in warm acetic acid. On keeping, crystalline needles of a substance settled out, which proved to be of protein nature. All subsequent attempts to again obtain the protein from the urine in crystalline form were unsuccessful.

The needle-shaped crystals contained nitrogen and sulphur, gave positive Millon's, Molisch, Ehrlich, biuret and xanthoproteic reactions, dissolved in dilute acids and alkalis, and in their general behaviour closely resembled the crystals of "Bence-Jones" protein described by Grutterink and de Graaff (A., 1906, i, 326). Post-mortem examination showed that the pathological changes in the bone marrow usually associated with the "Bence-Jones" albuminuria were absent.

H. W. B.

**The Iodine Content of Tuberculous Tissues.** PAUL A. LEWIS and ROBERT B. KRAUSS (*J. Biol. Chem.*, 1914, 18, 313—317).—Tuberculous tissue derived from animals to which no iodine preparation has been knowingly administered may contain amounts of iodine very appreciably higher than normal control tissue of the same animal. The statement that tuberculous tissue in animals

treated with iodine products may store up iodine must therefore be accepted with reserve. H. W. B.

**Retention of Nitrogen by Administration of Ammonium Salts or Urea, investigated by Permanent Intravenous Injection Experiments.** V. HENRIQUES and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1914, 92, 21—45. Compare Grafe, 1913, A, 125, 547, 1128).—The experiments were carried out on goats and turkeys with cannulae permanently inserted into peripheral veins, by means of which sugar, sodium acetate, sodium citrate, and simple nitrogenous substances, such as urea and ammonium acetate, were administered to the animals day by day. In this way, the possibility of synthetic action through the agency of bacteria in the intestine was avoided. The results showed that a permanent retention of nitrogen in the body was in no case achieved, and the conclusion drawn is that the nitrogen retention on feeding with urea and ammonium salts, observed by Grafe and others, was due to the action of bacteria in the alimentary canal or to a simple retention of these substances in an unaltered form in the body.

H. W. B.

**Reversible Paralysis of Peripheral Nerves by Acids and Salts.** FRIEDRICH HACKER (*Zeitsch. Biol.*, 1914, 64, 224—239).—Injection of dilute inorganic or organic acids temporarily paralyses the neighbouring peripheral nerves, as evidenced in man by the local anaesthesia produced, and in frogs by the increase of the threshold stimulus of the sciatic nerve. The extent of the paralysis is largely dependent on the concentration of hydrogen ions. When bases are injected, hyperalgesia results as a secondary effect of the contemporary hyperaemia. Salts which are partly hydrolysed in solution exert on injection the same action as the stronger ion. The weak local anaesthetic action of morphine hydrochloride is not due to the morphine, because when coupled with a weaker acid no anaesthesia is produced. The analgesic action of potassium sulphate is due to the potassium ion. In practice, the use of magnesium sulphate, or, better, chloride, is preferred, because these salts on injection produce less injury to the tissues and no pain.

H. W. B.

**The Pharmacological Action of Acids which Precipitate Calcium and of Magnesium Salts.** E. STARKENSTEIN (*Arch. exp. Path. Pharm.*, 1914, 77, 45—82).—Similar toxic effects are produced by the administration to rabbits of any of the following substances, which form precipitates with calcium ions: oxalic acid, sodium salts of ortho-, pyro-, and meta-phosphoric acids, sodium inositol-phosphate (phytate), and sodium fluoride. Animals showing intense toxic symptoms as the result of lethal doses of these substances may nevertheless recover if calcium chloride is injected. Conversely, a preliminary injection of calcium chloride renders these substances innocuous. The toxic symptoms are lowering of

blood pressure, rise of temperature, and slowing of the heart, with eventual arrest in diastole.

Phosphates and phytates inhibit blood clotting in a similar manner to oxalates and fluorides. Addition of magnesium salts restores the clotting property of the blood. Mixtures of salts of calcium-precipitating acids and magnesium salts, and the soluble magnesium salts of oxalic and metaphosphoric acids, do not exert any toxic action. As these salts and salt mixtures precipitate the calcium ion, it follows that the magnesium ion can replace the calcium ion in certain of its functions in the body, and the toxic action of acids which precipitate calcium is due to the withdrawal of calcium ions, and not to the respective anions. H. W. B.

**The Action of Iodine in the Animal Body.** LEO ADLER and LUDWIG CZAPSKI (*Biochem. Zeitsch.*, 1914, 65, 117—128).—It has been shown by Adler that the injection of iodine in potassium iodate (Lugol's solution) can lead to an injury to the testicles, resulting, with the correct dose, in a complete destruction of the parenchyma. The same result cannot be produced by potassium iodide alone. Experiments were carried out on rabbits with the object of throwing light on this action. The iodine in various tissues was estimated after injection both of the iodine alone and of the iodate containing free iodine. After both injections, however, the iodine was found in inorganic form in testicles and other organs, and not combined with any organic substance. In no case could any iodine derivative of a protein be detected. So far, the results offer no explanation of the characteristic action of solutions containing free iodine. S. B. S.

**The Synthesis of Hippuric Acid in the Animal Organism.**  
**II. The Synthesis and Rate of Elimination of Hippuric Acid after Benzoate Ingestion in Man.** HOWARD B. LEWIS (*J. Biol. Chem.*, 1914, 18, 225—231. Compare this vol., i, 774).—In man, after the administration of from 6 to 10 grams of sodium benzoate, elimination as hippuric acid takes place very rapidly, 85 to 90% of the ingested benzoate being excreted in from five to six hours. The rate of elimination of hippuric acid after the administration of sodium benzoate is only slightly less rapid than after the administration of hippuric acid. After benzoate ingestion, the urine collected during the first six hours, the period during which the greater part of the hippuric acid is being excreted, has a lower urea + ammonia content than in a normal control period, indicating that hippuric acid nitrogen is derived at the expense of the nitrogen normally eliminated as urea. H. W. B.

**The Action of Caffeine on Striped Muscle.** KNUD J. A. SECHER (*Arch. expt. Path. Pharm.*, 1914, 77, 83—121).—Perfusion with 1:30,000 caffeine solution produces histological changes in the voluntary muscle fibres of the frog similar to those brought about by xanthine, theobromine, and theophylline. Similar results are obtained with birds and mammals, but only with solutions of

much greater concentration (up to 2%). Caffeine in low concentration increases contractility of the muscle, but the work done is increased only when the muscle is unsupported. H. W. B.

**The Behaviour of Sodium Formaldehydesulphite (Hydroxymethanesulphonate) in the Organism; its Applications to Therapeutics.** FRIEDRICH SIMON (*Biochem. Zeitsch.*, 1914, 65, 71—106).—This substance can be tolerated in relatively large doses. Thus, a man can take 9 grams within fourteen hours, and a dog 30 grams within three days, and rabbits doses equivalent to 1 gram per kilo. of body-weight, without ill-effects. The scission of the compound takes place very rapidly in the blood stream, and formaldehyde can only be detected in the blood in the first few minutes after intravenous injection. Neither the unchanged drug nor formaldehyde could be detected in the urine. There is no evidence that the drug possesses any value either as solvent for uric acid or as a urinary disinfectant. As an antidote to phenol (in experiments on rabbits) it is unable to counteract the final action of a lethal dose, but with smaller doses it can counteract or lessen the duration of the convulsions. It can increase the power of the organism to reduce methylene-blue. S. B. S.

**Some Physiological Properties of Galegine Sulphate.** GEORGES TANRET (*Compt. rend.*, 1914, 159, 108—111. Compare this vol., i, 721, 859).—Galegine in the form of its sulphate has a toxic effect both on cold- and warm-blooded animals. In the case of the frog, 0.02 to 0.03 gram injected into the peritoneum produces total paralysis in ten to fifteen minutes, with abolition of the reflexes. The respiration ceases at the end of one hour, whilst the heart only ceases to beat after several hours. With the guinea-pig, death ensues fifteen minutes after hypodermic or intraperitoneal injection of 0.23 to 0.26 gram per kilogram of live-weight, fifty-five minutes after 0.1 gram, and 105 to 130 minutes after 0.03 to 0.05 gram. A guinea-pig resists an injection of 0.01 to 0.02 gram of the sulphate per kilogram of live-weight. The rabbit is slightly more resistant than the guinea-pig, whilst the dog comes between them. In all cases the first effect is to produce paralysis of the medulla and nerve centres, followed by asphyxia, the cardiac muscle in all cases surviving the cessation of respiration. Galegine sulphate has no hæmolytic action, but in feeble dose the injection is followed by a short, rapid lowering of the blood pressure, and then a gradual and continuous rise, reaching 4–5 cm. of mercury in five to six minutes, returning to its original value after twenty minutes. With toxic doses, the pressure diminishes at the end of a very short time, falling more or less rapidly, and does not reascend. W. G.

**Action of Hydroxyquinoline and Certain of its Derivatives on Purine Metabolism.** FELIX BOENHEIM (*Chem. Zentr.*, 1914, 1685; from *Zeitsch. expt. Path. Ther.*, 15, 379—384).—The effect of 8-hydroxyquinoline-*o*-acetoxybenzoate, "8-hydroxyquinoline-

glycerol ether, and hydroxyquinoline hydrochloride on the elimination of uric acid and allantoin in dogs has been investigated. Small doses of 8-hydroxyquinoline-*o*-acetoxybenzoate have no effect, whilst the quantity of uric acid is slightly diminished and that of allantoin increased after medium doses; quantities of 5 grams have a similar effect, whilst, after 10 grams, an appreciable diminution of allantoin occurs on the first day. A toxic action is not observed. "8-Hydroxyquinoline glycerol ether" causes an increase in the uric acid, a diminution in the allantoin elimination. Ethyl phenyl-cinchonate brings about a slight diminution in the uric acid and increase in allantoin, whilst hydroxyquinoline causes a decrease in uric acid and in allantoin. H. W.

**Chemical Study of Certain Causes of Poisoning by Carbon Monoxide.** E. KOHN-ABREST (*Ann. Falsif.*, 1914, 7, 292—304).—Carbon monoxide may be introduced into the atmosphere from sources such as charcoal furnaces, internal-combustion engines, gas stoves, etc., and analyses are recorded showing the composition of the gases produced in these cases. The gases from a charcoal fire may contain up to 1.8% of carbon monoxide, those from a petrol engine 7.32% (in these gases the quantity of carbon monoxide exceeds that of the carbon dioxide), whilst the combustion products from gas heaters contain from 1 part in 15,000 to 0.3% of carbon monoxide, according to the supply of air to the burner. The cumulative action of carbon monoxide on the animal system emphasises the necessity of thorough ventilation when any of the above-mentioned sources of heat are employed. W. P. S.

**The Bases of Gas-works Coal-tar which are believed to be the Predisposing Cause of Pitch Cancer, with Special Reference to their Action on Lymphocytes, together with a Method for their Inactivation. I. Auxetic Action.** DONORNY NORAS (*Biochem. J.*, 1914, 8, 253—259).—Coal-tar from gas-works contains certain bases which excite division of blood lymphocytes and other living cells (auxetic action), leading to ulcers and epithelioma among the workmen employed. The auxetic bases have been extracted with 5% hydrochloric acid, and isolated in the form of their crystalline picrates. Picrate A has m. p. 199—201° and empirical formula  $C_{22}H_{14}O_4N_6$ , and is less soluble in alcohol than picrate B, m. p. 161—162°. Hydrolysis of picrate A yielded a small quantity of active auxetic base. A practical method, applicable on the large scale, of inactivating these bases in the tar is described, depending on the rapid loss of auxetic power on oxidation by air. H. W. B.

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## Chemistry of Vegetable Physiology and Agriculture.

Comparative Investigations on the Action of Chemico-therapeutic Preparations and Other Antiseptics on Bacteria. O. SCHIEMANN and T. ISHIWARA (*Chem. Zentr.*, 1914, i, 1449—1450; from *Zeitsch. Hyg. Infekt.-Krankh.*, 1914, 77, 49—100).—The drugs salvarsan and ethylhydrocupreine are powerful antiseptics *in vitro*; experiments in bouillon show that their power of checking development, like that of mercuric chloride, extends to a dilution of 1 in 500,000 to 1 in 1,000,000. The bactericidal action of salvarsan is noticeable at about the same dilution. In comparison with other antiseptics, the action of these substances is highly selective. At the given dilution, salvarsan is only active towards the bacilli of dysentery, splenialgia, and glanders, ethylhydrocupreine towards pneumococci; the action towards other bacilli is one hundred to one thousand times weaker and slower. In all cases investigated, the action *in vivo* corresponds with that *in vitro*. The selective action of the chemiotherapeutic preparations on the above bacteria is approximately as powerful *in vitro* in serum as in bouillon, and actually better in active than in inactive serum. Sublimate behaves in the opposite manner. Phenol is much less weakened by serum than is sublimate. The action of salvarsan is not identical in all sera; thus, it is noticeably weaker in ox serum than in rabbit serum. The opposed behaviour in active serum of salvarsan and ethylhydrocupreine on the one hand, and sublimate on the other, points to an action of the labile components of serum, such as lipoids and lipoid albuminoids, during disinfection *in vivo*. A considerable weakening of the antiseptic action of salvarsan, sublimate, and phenol in bouillon is caused by the addition of lecithin or cholesterol in considerable concentration (1:100). With regard to the quantitative relationship between the amounts of bacteria and antiseptic, the latter is found to increase disproportionately with the former. With similar concentrations of disinfectant and similar seeding, larger volumes of sublimate or salvarsan solutions showed somewhat more powerful actions, both bactericidally and in the prevention of development. In respect of these quantitative relationships, no distinct difference could be perceived between salvarsan, sublimate, and phenol. H. W.

Behaviour of Bacteria, Yeasts, and Moulds towards Iodine Compounds. ALEXANDER KOSSOWICZ and WALTER LOEW (*Bied. Zentr.*, 1914, 43, 359; from *Zeitsch. Gärungsphysiol.*, 1913, 2, Heft 3).—With different varieties of pure yeasts grown in sugar solutions containing potassium iodide, no separation of iodine occurred. Similar results were obtained with most of the moulds employed. On the other hand, there was a considerable separation of iodine in cultures of *Penicillium glaucum* and *Aspergillus niger*, and also, in more prolonged experiments, with *Cladosporium herbarum*.



The positive results obtained with yeasts by Bokorny (A., 1912, ii, 1201) are attributed to the presence of bacteria.

N. H. J. M.

#### Decomposition of Formates by *Bacillus coli communis*.

EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1914, [B], 87, 461—471).—The power of *B. coli communis* to decompose formic acid varies considerably when the organism has been kept on artificial media. A very small excess of acid or alkali inhibits the decomposition of formates, and addition of dextrose greatly increases the decomposition, owing to the neutralisation of the alkali of the formate by the acid produced from the sugar.

Formates may be conveniently employed as neutralising agents; the activity of gas-forming organisms is considerably increased.

A method is described, with sketch, by which the decomposition of various substances by micro-organisms, in 50—100 c.c. of solution, may be followed quantitatively.

N. H. J. M.

#### Enzymes which are Concerned in the Decomposition of Dextrose and Mannitol by *Bacillus coli communis*.

EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1914, B, 87, 472—484).—Whilst artificially selected strains of *B. coli communis* did not lose the enzymes which cause the final reaction in the production of alcohol and acetic acid, there was an absence or diminution of the reducing mechanism of the cell, so that some intermediate substance, from which formic acid and the precursor of alcohol and acetic acid are derived, cannot be readily decomposed.

N. H. J. M.

**Influence of Organic Substances on Nitrification and Denitrification in Soils.** CHR. BARTHEL (*Bied. Zentr.*, 1914, 43, 372—373; from *Medd. Centralanst. förskökärs. Jordbr.*, 1913).—The results of experiments in which ammonium sulphate and various organic substances were added showed that the extent to which nitrification was hindered by the different substances diminished in the following order: peptone, asparagine, acetamide, ammonium acetate, carbamide. So that, in accordance with the previous results of Winogradski and Omelianski, the inhibiting action on nitrification disappears more or less quickly, according to the rate of decomposition of the organic substance employed.

Dextrose and other readily soluble non-nitrogenous substances have a distinctly retarding effect on nitrification, even when only small amounts are present.

Whilst soils rarely contain sufficient soluble organic matter to retard nitrification, the activity of nitrifying organisms is almost completely checked in manure heaps.

N. H. J. M.

#### The Formation of Acetaldehyde in Alcoholic Fermentation.

S. KOSTITSCHKEV (*Biochem. Zeitsch.*, 1914, 64, 237—250).—The author replies to a criticism of Neuberg and Kerb (this vol., i, 118) of their work (A., 1912, i, 323) on the increased production of acetaldehyde by fermentation with yeast in the presence of zinc

chloride. He incidentally shows that alcohol can be estimated by Nicloux's method when aldehyde is present if the mixture is distilled in a vacuum (at 30—35°) over sodium hydrogen sulphite, to separate the aldehyde.  
S. B. S.

**The Part Played by Acetaldehyde in Alcoholic Fermentation.**  
C. NEUBERG and J. KERN (*Biochem. Zeitsch.*, 1914, 64, 251—256).—  
A detailed reply to Kostytshev (see preceding abstract).  
S. B. S.

**Can the Phenomenon of Thermo-regeneration be Extended to the Different Diastases of Yeast.** GABRIEL BERTRAND and M. ROSENBLATT (*Compt. rend.*, 1914, 158, 1823—1826).—Maltase and catalase obtained from slightly autolysed bottom yeast do not undergo thermoregeneration in the same way as invertase (compare this vol., i, 909). The activity of both of these enzymes is destroyed by heating their solution to 70°, and is not restored by heating for one minute at either 80°, 90°, or 100°. W. G.

**The Enzymes of Washed Zymin and Dried Yeast (Lebedev). III. Peroxydase, Catalase, Invertase, and Maltase.** ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1914, 8, 217—226).—Fresh English yeast gives the peroxydase coloration with hydrogen peroxide and *p*-phenylenediamine. After drying at 38°, the yeast, on suspending in water, no longer gives a positive reaction for peroxydase, owing to the presence of an inhibiting agent produced during the drying process. By repeatedly washing the dried yeast, the inhibiting agent is removed and the apparent peroxydase content restored.

Washing does not affect the activity of the catalase of dried yeast. Invertase and maltase are not readily removed from dried yeast by washing, the power of hydrolysing sucrose being reduced after six washings by a third, whilst that of hydrolysing maltose is scarcely affected.  
H. W. B.

**Assimilation of Elementary Nitrogen by Yeasts and Moulds.** ALEXANDER KOSSOWICZ (*Biochem. Zeitsch.*, 1914, 64, 82—85).—From experiments on the growth of various moulds and yeasts in nitrogen-free media, the conclusion was drawn that these organisms cannot assimilate elementary nitrogen. A minute amount of nitrogen could be detected in the cultures when in contact with air from which nitrogen compounds had not been removed. No such increase could be found, however, when the air in contact with the cultures had been purified in such a way as to exclude the small amount of nitrogen compounds it is apt to contain.  
S. B. S.

**Synthesis of Nitrogenous Substances in Yeast Juice Obtained by Maceration.** S. KOSTYTSHEV and W. BRILLIANT (*Zeitsch. physiol. Chem.*, 1914, 91, 372—391).—The juice always contains a considerable quantity of proteins and endotryptase. Autolysis proceeds readily at 34°, and the hydrolysable proteins are all

decomposed in two days, but a small, constant amount of protein remains unattacked even after nine days. After hydrolysis of the proteins, synthetic processes may occur, the necessary conditions being a sufficient amount of decomposed protein and a high concentration of sugar. Subsequently, the nitrogenous products precipitable by Stutzer's method with copper hydroxide is found to be increased. The increase may amount to 16% of the quantity present before autolysis. Precipitation of these nitrogenous substances with basic lead acetate gives considerably lower values.

R. V. S.

**Formation of Chemical Compounds during the Destruction of Yeast Organisms by Different Chemical Agents.** With-drawal of the Agents from Solution. TH. BOKORNY (*Chem. Zentr.*, 1914, i, 1363—1364; from *Allg. Brauer-u. Hopfenzeit.*, 54, 541—544, 567—569, 583—585, 592—594).—A chemical compound between the poison and the yeast cell is formed when the latter is killed by chemical agents. The concentration of poison in the solution is in most cases considerably diminished by the introduction of living yeast. The death of the cell appears to occur before the union of poison and protoplasm ceases. A table is given showing the quantities of the following substances which in *N*, *N*/10, and *N*/100-solution combine with 20 grams of living yeast in twenty-four hours, namely, ammonia, sodium hydroxide, sulphuric acid, formic acid, hydrofluoric acid, hydrazine hydrate, iodine, sulphurous acid, oxalic acid, and acetic acid. Combination is observed in all cases except with formic acid, which appears to function as a contact poison. Further, magenta, indine-violet, methyl-green, malachite-green, tropäoline, eosin, chrysoidine, Victoria-blue, and dianyl-black are found to combine with yeast. Aniline dyes, particularly those which possess a great capacity for dyeing, are found to have a poisonous action even at a dilution of 1 in 100,000, that is, at a dilution at which the most powerful poisons are ineffective.

H. W.

**The Oxidation and Reduction Processes Taking Place at the Expense of the Water Produced by Killed Yeast.** W. PALLADIN and E. LOVTSCHINOVSKAJA (*Biochem. Zeitsch.*, 1914, 65, 129—139\*).—The experiments were carried out with the object of testing further the views of Palladin as to the part played by water in biological oxidation and reduction processes in the presence of a hydrogen acceptor. In confirmation of the results of Neuberg and of von Lebedev, it was found that the killed yeast can destroy potassium gluconate. The presence of methylene-blue largely increases the amount of carbon dioxide evolved in the reaction. This fact leads to the assumption that yeast contains a reduction ferment which is able, in the presence of a hydrogen acceptor, to decompose organic acids, with evolution of carbon chloride. The same result was observed in the case of lactic acid. Potassium glycuronate is also decomposed by the yeast, but in this

\* and *Bull. Acad. Sci. St. Petersburg*, 1914, [iii], 8, i, 749.

case methylene-blue inhibits the reaction. Saccharic acid is also decomposed, but in this instance the process is not stimulated by the dye. The decomposition of the gluconic and lactic acids in the presence of methylene-blue is the first instance of the artificial conversion of a fermentation into a respiration process.

S. B. S.

**The Protein Substances of *Aspergillus niger*.** PIERRE THOMAS and ROBERT C. MORAN (*Compt. rend.*, 1914, 159, 125—127).—Using the method employed for the examination of yeast (compare A., 1913, i, 942), the authors have isolated from *Aspergillus niger* two protein substances corresponding with those obtained from yeast. The one is easy to isolate, being insoluble in water, sparingly soluble in 10% sodium chloride solution, soluble in aqueous sodium hydroxide, ammonia, alkali carbonates, or lime-water, and from these solutions is precipitated by mineral acids. It contains 12.3—12.9% nitrogen, 0.7% phosphorus, and 0.5—0.6% sulphur. It gives the xanthoprotein reaction, the biuret reaction, Hopkins' glyoxylic reaction, and reacts with Millon's, Molisch's, and the Ehrlich-Pröschner reagents, the latter showing the presence of glucosamine. With hydrochloric acid in the cold it gives a green coloration, which slowly passes to the ordinary Liebermann violet colour. On careful warming with orcinol hydrochloride it gives a purple precipitate and a green liquid, and with phloroglucinol hydrochloride an abundant, deep red precipitate. It gives no coloration on boiling with an alkaline solution of lead oxide. Using the modified Hausmann's method of hydrolysis (compare A., 1913, i, 1026) for determining the division of the nitrogen, the substance is found to contain less diamino- and more monoamino-nitrogen than the corresponding compound obtained from yeast. From its properties and analysis, it appears to be closely allied to casein, and to be derived from a nucleoprotein existing in the cells of the mould.

The second compound is a coagulable albumin, but occurs in too small a quantity to allow of it being characterised at present.

W. G.

**Organic Antiseptics which are Attacked by Micro-organisms.** S. CONDELLI (*Chem. Zentr.*, 1914, i, 1208; from *Staz. speriment. agrar. ital.*, 1913, 47, 85—94).—A culture solution containing mandelic acid was seeded with *Penicillium glaucum*, but a resolution of the acid could not be observed, although the organism developed readily; parallel experiments with *Aspergillus niger* showed a slight resolution. In a further series of experiments the mandelic acid was replaced by sodium benzoate, phenylacetic acid, and amygdalin respectively. After seeding with *Aspergillus niger*, a copious growth was observed after a few days in the solution containing the benzoate, followed in point of time by the solution containing amygdalin, and finally by that containing phenylacetic acid. Finally, it was shown that the percentages of benzoic acid, phenylacetic acid, mandelic acid, and amygdalin decomposed were 5.62, 6.26, 7, and 23.53 respectively.

H. W.

**The Soluble Polysaccharides of Lower Fungi. I. Mycodextran, a New Polysaccharide in *Penicillium Expansum*.** ARTHUR W. DOX and RAY E. NEIDIG (*J. Biol. Chem.*, 1914, 18, 167—175).—Mycodextran has been prepared by extracting large quantities of this mould (which occurs characteristically on decaying apples) with boiling water. On cooling, the clear extract deposited the new polysaccharide in an impure form, and by repeated reprecipitation by alcohol from its aqueous solution, and finally drying in a vacuum, it was obtained as a fine powder containing 0.09% ash, and giving no colour reaction with iodine. The dry powder swells in cold water, and on warming dissolves to a clear solution. If 1% of the substance is present, a stiff, white paste results on cooling. It is soluble in cold sodium hydroxide and in hydrochloric acid, insoluble in ammonia, acetic acid, and sodium carbonate. It has  $[\alpha]_D^{20} + 251^\circ$ , and  $n_D$  0.00131. The empirical formula is  $C_6H_{10}O_5$ , and on hydrolysis it gave only dextrose, which was recognised by the polarimeter, Fehling's solution, and the preparation of glucosazone.

The ordinary amylolytic enzymes were without action on mycodextran.

H. W. B.

**The Toxin of *Rhizopus Nigricans*.** ROSS AIKEN GOETNER and A. F. BLAKESLEE (*Amer. J. Physiol.*, 1914, 34, 353—367).—The toxic substance of *Rhizopus Nigricans* has been obtained in an impure state by precipitation of an aqueous extract of the mould with alcohol. The product gives the reactions for protein and carbohydrate. It is slowly destroyed by boiling its aqueous solution, and more rapidly by boiling with  $N/10$ -hydrochloric acid. Peptic digestion for three hours is without effect on the toxicity.

In intravenous injections into rabbits, the lethal dose is about 1:250,000 parts of body-weight; but large doses may be given by the mouth without any harmful effect being observed.

H. W. B.

**Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds.** FRANKLIN KIDD (*Proc. Roy. Soc.*, 1914, B, 87, 408—421, 609—625).—The results of experiments with various seeds showed that germination is retarded or inhibited by high partial pressure of carbon dioxide. Whilst some seeds, such as beans, cabbage, barley, and peas germinate at once when the carbon dioxide is removed, other seeds fail to germinate until they have been completely dried and re-wetted, or the germinating power may be restored by removing the testa. In this class of seeds it seems that the permeability of the testa is diminished under the influence of carbon dioxide, and this would result in a reduced amount of oxygen reaching the embryo, and in a relative rise in the carbon dioxide pressure in the embryo tissues.

An experiment was made in which a layer of fresh grass (7.5 cm.) was covered with 45 cm. of soil, in which a week later seeds were buried at depths of 7.5, 15, and 22.5 cm. After seven

days it was found that only three out of twenty-five of the seeds 7.5 cm. deep had sprouted, and that all the seeds at the lower depths failed to germinate. In a control experiment, without grass, all the seeds germinated. Two weeks after the pit containing grass was made, it was found that the air from 15 and from 30 cm. below the surface contained, respectively, 16.5 and 20.0% of carbon dioxide.

The inhibitory value of given carbon dioxide pressures is increased by low temperatures and by a low supply of oxygen, and diminished by a rise of temperature and an increased supply of oxygen.

In the case of seeds such as *Hevea Brasiliensis*, which rapidly deteriorate, the carbon dioxide produced by respiration in a closed flask rose to 40%; seeds kept in this manner showed a marked increase in vitality.

Both the arrested development of moist maturing seeds on the plant, and the retarded germination of moist resting seeds under apparently suitable conditions of temperature, moisture, and supply of oxygen, are connected with an inhibitory partial pressure of carbon dioxide in the tissues of the embryo. N. H. J. M.

**Action of Carbon Tetrachloride and Carbon Disulphide Vapours on the Germinating Power of Seeds.** RIEHM (*Bied. Zentr.*, 1914, 43, 358; from *Mitt. K. Biol. Anst. Land-u. Forstwirts.*, 1913, 14, 25).—Whilst hemp and barley were found to be greatly injured, rape is more resistant. The effect on maize varied considerably with different varieties. Carbon disulphide acts more quickly than carbon tetrachloride. N. H. J. M.

**Absorption of Ions by Plants.** F. PLATE (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 839—844).—The paper describes a series of quantitative experiments with *Triticum sativum* and *Hyacinthus orientalis* grown in solutions containing one of the following salts: manganese chloride, manganese bromide, manganese nitrate, and manganese sulphate. Anion and cation are absorbed in the same proportion as that in which they exist in the solution; the anion chiefly reaches the shoot, whilst the cation is found especially in the root. R. V. S.

**Influence of the Continuous Electric Current on the Absorption of Nutritive Substances by Plants.** D. CROUCHAK (*Compt. rend.*, 1914, 158, 1907—1910).—In order to investigate the causes producing the variation of absorption of a nutritive substance by roots of a plant with changes in the medium in which the roots are immersed (compare A., 1913, i, 801), the author has examined the influence of an electric current. A number of young wheat plants were threaded on a fine platinum wire and plunged into the nutritive solution. A second wire was immersed in the solution, and the two connected to the poles of a battery giving a current intensity of 0.5 to 250 millionths of an ampere. At the end of the experiment the amount of the nutritive elements

absorbed were determined. Similar experiments were performed to measure the adsorption by the roots of plants, killed by immersion in boiling water for ten minutes. The current, according to its intensity and direction, produces a variation in the velocity of absorption of cations and anions. In the case of the cations, the velocity is constant when the plants are connected to the positive pole, but increases at first very rapidly with the current intensity to a certain point, after which it is almost constant, when the plants are connected with the negative pole. The inverse is true for anions. This variation is not due to electrolysis, since the increase in absorption is greater than can be accounted for by the increased number of ions liberated, due to the increased current. The velocity of adsorption by roots of dead plants is influenced in the same sense by the electric current.

W. G.

**The Study of Plant Enzymes, particularly with Relation to Oxidation.** A. D. HALL, E. F. ARMSTRONG, H. E. ARMSTRONG, F. KEEBLE, and E. J. RUSSELL (*Rep. Brit. Assoc.*, 1913, 143-145).—A short report of work published during 1913.

C. H. D.

**The Velocity of Hydrolysis and Displacement by Water of the Nitrogenous and Mineral Substances Contained in Leaves.** G. ANDRÉ (*Compt. rend.*, 1914, 158, 1812-1815. Compare A., 1913, i, 233, 431).—The author has determined the amounts of nitrogenous matter, expressed as nitrogen, phosphorus expressed as  $H_3PO_4$ , and potassium expressed as  $K_2O$ , passing by exosmosis from the leaves of chestnut trees immersed in water for one, two, and six months, the leaves being taken: (a) when quite young; (b) at the period of flowering; (c) at the time of maturity of the fruit. The exosmosis of nitrogen is small even at the end of six months, varying from 6.32% of the total nitrogen in young leaves down to 2.0% in the oldest leaves. The amount of nitrogen passing out from the leaf after the first month is almost a constant percentage of the total passing out, independent of the age of the leaf. The exosmosis of phosphorus is greater, corresponding with rather more than 50% of the total amount in the leaf, and does not appear to vary with the age of the leaf. The amount of phosphorus passing out in the first month's immersion, expressed as a percentage of the total passing out in six months, decreases regularly with the age of the leaf. Potassium is the element which passes out to the greatest extent, varying from 97.85% of the total in the young leaves to 87.2% of the total in the oldest leaves. As in the case of phosphorus, the loss during the first month diminishes with the age of the leaf.

W. G.

**Absorption of Certain Radicles by Leaves in Varying Stages of Decay, and the Effect of Leaves on the Absorption of these Radicles by a Soil.** H. A. NOYES (*J. Ind. Eng. Chem.*, 1914, 6, 574-576).—Leaves, undecayed and in varying stages of decay, show absorption for certain radicles, particularly ammonium,

potassium, and calcium, and phosphoric and sulphuric acids, but not for chlorine, bromine, iodine, nitric acid, or magnesium. The addition of soil to the leaves does not inhibit the absorption, but in the case of mixtures of leaves and soil the absorption does not proceed on the same basis as with the constituents separately.

W. P. S.

**The Nitrogenous Constituents of Plant Galls. I**  
M. NIERENSTEIN (*Zeitsch. physiol. Chem.*, 1914, 92, 53–55).—Galls from *Quercus Aegilops*, L., were extracted with benzene or carbon tetrachloride, and, after distilling off the solvents, the residues deposited, in the course of two and a-half years, 9 grams of crystalline material, which, on recrystallisation from alcohol, had m. p. 234–238° (decomp.). The substance is probably 1-galloyl-leucine,  $C_{16}H_{17}O_6N$ , and has  $[\alpha]_D^{20} - 57.35^\circ$ . The structural formula is probably  $CHMe_2 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot C_6H_2(OH)_3$ .

On hydrolysis, gallic acid and *dl*-leucine were obtained and identified.

H. W. B.

[The Araliaceæ Family, with Special Reference to the Glucosides and Oxydases of the Leaves of *Polyscias nodosa*, Forst, and *Hedera Helix*. L....] JOS. HALBERKANN (*Arch. Pharm.*, 1914, 252, 187–190).—In reply to van der Haar (this vol., i, 122), the author states that several observers have recorded the production of arabinose from saponins, and also that neither he nor van der Haar has sufficiently characterised as sesquiterpenes the hydrocarbons obtained by the dry distillation of sapogenins.

C. S.

**The Enzyme of Chelidonium Seeds. II.** KONRAD BOURNOT (*Biochem. Zeitsch.*, 1914, 65, 140–157).—Further details of the preparation and properties already described (*A.*, 1913, i, 920) of the chelidonium lipase are given. When free from oils, the dry powder loses part of its lipolytic activity by grinding. A very active powder can be obtained when the oil-containing seeds are allowed to remain with light petroleum; this separates in a fine state, and can be readily separated from the coarser particles. The oil obtained in this process, when the petroleum is distilled off at 20°, also has lipolytic properties, which it readily loses on warming to 30°. The ester-forming action on mixtures of monohydroxy-alcohols and fatty acids was studied, and when equivalent amounts of acid and alcohol were used, synthesis amounted to as much as 83.5%, which was not largely increased by excess of alcohol. With glycerol, on the other hand, the synthesis was furthered when excess of the alcohol was present and a little water was added; 78% of the acid could then be esterified. A comparison was made of the esterification of oleic acid by various alcohols; most of the primary monohydroxy-alcohols form esters readily (37 to 91%); the secondary and tertiary alcohols form esters with greater difficulty or not at all (for example, tertiary amyl alcohol). The polyhydroxy-alcohols do not esterify so readily, the maximum lying between 42 and 59%. The esterification of a large number of acids



by isobutyl alcohol was also studied. The author describes the preparation of  $\beta$ -mono-olein,  $C_5H_9O(OH)_2 \cdot C_{18}H_{33}O$ , m. p. 26°, and of isobutyl heptate, b. p. 209°, D<sub>4</sub> 0.8593, by means of the enzyme. S. B. S.

**Plant Ferments. I. The Oxydases of the Maize Cobb.** G. DOBY (*Biochem. Zeitsch.*, 1914, 64, 111—124).—The style of the cobb owes its coloration to the presence of a peroxydase and oxygenase; a tyrosinase is absent. The peroxydase has a heat-stable zymogen; it is not a protein, but a non-reducing polysaccharide, which is soluble in water. The preparations contained 5 or more % of ash, in which manganese could not be detected. The peroxydase is readily injured by higher concentrations of hydrogen peroxide, and its action is impeded by the presence of sugars and carbohydrates. The oxygenase is always present in the styles, but is absent in the grains and axes, which contain, however, a peroxydase. Furthermore, the peroxydase continually increases in quantity in the styles, whilst no marked change in amount is observed in the grain and axes. The physiological significance of these facts is discussed by the author. The oxygenase also increases in quantity in the styles, but not so rapidly in proportion as the peroxydases. S. B. S.

**Morphology and Microchemistry of Podophyllum peltatum.** O. TUNMANN (*Pharm. Zentr.-h.*, 1914, 55, 619—623).—Podophyllotoxin occurs fairly regularly in all the parenchymatous cells of the rhizome, whilst the resinous portions of the podophyllin are found in the adjacent, excretory cells. The presence of quercetin can be detected, by sublimation, in as little as 0.1 to 0.2 gram of podophyllum (drug). The first sublimate consists of fatty drops with crystals of fatty acids and phytosterols; this is followed by tarry substances, and finally by quercetin. Quercetin is not specially localised in the cork and bark, but seems to accompany the podophyllotoxin. N. H. J. M.

**Dependence of the Relation of Lime and Magnesia on the Concentration.** P. L. GILLE (*Porto Rico Exper. Stat. Bull.*, 12, 1913).—Water-culture experiments with rice in which calcium and magnesium were supplied in various relations to each other and to the other nutrients. In the presence of small amounts of all other foods, solutions of equal percentage amounts of calcium and magnesium chlorides seem to have the same toxic effect. In concentrated solutions of calcium chloride, containing small amounts of the other nutrients, the growth of rice is considerably increased by a slight increase in the amount of magnesium chloride.

In solutions of 172 to 109 per 100,000 of calcium and magnesium chlorides, with minor amounts of all other nutrients, growth was distinctly better when the bases lime and magnesia were present in the ratio 1:1 than in the ratio of 10:1, 5:1, 1:5, or 1:10. In solutions of 62 to 23 per 100,000 of the combined chlorides, the growth of rice seemed to be unaffected by the ratio of lime to magnesia between ratios of 10:1 and 1:10.

The results show that rice differs from many plants in being

relatively less sensitive to magnesium chloride. Whilst the ratio has an effect at comparatively high concentrations, it does not, within the limits of the experiments, at low concentrations.

The conclusion is drawn that the toxicity of an excess of lime or magnesia is not due simply to an unfavourable proportion between the two salts alone, but to an unfavourable proportion between the salt which is in excess and all the other salts present. In ordinary soils the ratio of available lime and magnesia may be expected to be without effect. In alkali soils the ratio may be of the greatest importance.

N. H. J. M.

**Solubility of Soil Constituents.** HER. FISCHER (*Bied. Zentr.*, 1914, 43, 292—294; from *Intern. Mitt. Bodenk.*, 1913, 3, 331).—Indications were obtained of a suitable method for obtaining available potassium from sparingly soluble rocks, in which phonolite is fused with calcium carbonate and sodium chloride, the product ground, and extracted with water.

Experiments are described in which the amounts of potassium dissolved by water, saturated with carbon dioxide, from biotite and phonolite were estimated. The solubility of biotite was found to be less than that of phonolite. On the other hand, Pfeiffer and Blanck found in experiments with oats that the potassium of phonolite is less available than that of biotite.

N. H. J. M.

**Decomposition of Silicates by Soil Bacteria.** K. BASSALIK (*Bied. Zentr.*, 1914, 43, 502; from *Zeitsch. Gärungsphysiol.*, 1913, 3, 15—42).—In experiments with a number of finely powdered minerals it was found that nepheline, magnesia, talc, and augite were the most readily attacked by *Bacillus extorquens*, which dissolved from 4 to 6% of the minerals. Butyric acid bacteria acted similarly, except that they decomposed apatite more readily. Nitrite bacteria acted comparatively vigorously, notwithstanding the slight production of acid.

N. H. J. M.

**Plastic and Adhesive Constituents of Clays.** A. ATTERBERG (*Bied. Zentr.*, 1914, 43, 295—301; from *Intern. Mitt. Bodenk.*, 1913, 3, 291).—From the results of experiments with a number of minerals, the conclusion is drawn that it is the particles which form scales which impart plasticity. In the case of the clays of northern Europe, biotite is the predominant plastic constituent, whilst in the case of the red soils in southern latitudes plasticity is chiefly due to hematite and limonite.

N. H. J. M.

**Microscopic Estimation of Soil-forming Minerals.** W. J. McCAGHEY and WILLIAM H. FRY (*Bied. Zentr.*, 1914, 43, 368—371; from *U.S. Dept. Agric. Bur. Soils. Bull.*, 91, 1913).—The minerals found most frequently and in greatest amounts are feldspars, albite and oligoclase being fairly well preserved, whilst the basic members of the group are more readily altered, and can frequently not be identified except in soils of the arid regions. Hornblende and epidote are the predominating minerals, and most of the soils contained tourmaline, rutile, and zircon. Apatite (fluorine apatite) was found in half of the soils, and garnet in ten.

Quartz frequently contains apatite, rutile, zircon, and gas, and sometimes liquids.

Soils derived from sandstone and slate formations vary very distinctly according to climatic conditions. In rainy districts quartz predominates, the other minerals being largely decomposed, whilst in arid regions the reverse is found.

The methods employed are described, and a detailed description of the minerals is given in the original paper.

N. H. J. M.

**Distribution of Certain Constituents in the Separates of Loam Soils.** L. A. STEINKÖNIG (*J. Ind. Eng. Chem.*, 1914, 6, 576—577).—Analyses of separates of varying coarseness, obtained by submitting the soils to sedimentation and centrifugal action, showed that the percentage of silica is greater, in all cases, than that of any other oxide; alumina is usually second in quantity, followed by iron. The proportion of silica diminishes from the coarser to the finer particles, and zirconia shows the same variation. Iron oxide, alumina, titanium, potash, and phosphoric acid increase in quantity in the finer particles. The distribution of soda, lime, and magnesia appears to follow no general rule.

W. P. S.

**Effect of Heat on Hawaiian Soils.** W. P. KELLEY and WILLIAM MCGEORGE (*Hawaii Agric. Exper. Stat. Bull.*, 30, 1913, 38 pp.).—Experiments on the effects of heating at 100° and 250°, and of ignition, on twelve different soils. Whilst the results varied a good deal, it was found that, on the whole, heating at 100° increases the amounts of manganese, calcium, magnesium, phosphoric acid, sulphates and hydrogen carbonates, and, in most cases, iron, soluble in water; in about half the soils the solubility of the potassium, aluminium, and silica was also increased.

The results obtained at the higher temperatures (250° and ignition) were similar, the increase in solubility being sometimes greater and sometimes less than that obtained at 100°.

The solubility in *N/5*-nitric acid was not altered much by heating at 100°. Heating at 250° sometimes considerably increased the solubility of aluminium, manganese, potassium, and phosphoric acid, and diminished the solubility of the calcium and magnesium.

The changes involved in heating soils are very complex and include, among others, flocculation, deoxidation of manganese dioxide, oxidation, particularly of iron, double decomposition, dehydration, and physical alterations of soil films.

The nitrates present in soils are practically all destroyed at 200—250°; whilst a decrease occurred at 100°.

Heating at 200° resulted in a loss of about 25% of the total nitrogen and in the production of abnormally large amounts of ammonia. The burning of brush in the field was found to cause a stimulation of ammonification, whilst nitrification was not restored in two months.

N. H. J. M.

## General and Physical Chemistry.

**Refractive Index at the Critical Point.** MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1914, 12, 282—288).—The refractive index at the critical point ( $n_c$ ) has been calculated from the equation  $(n_c^2 - 1)/(n_c^2 + 2) = R d_c$ , in which  $R$  is the refractivity and  $d_c$  the critical density. For aliphatic esters, alcohols, hydrocarbons, etc., the value of  $n_c$  obtained in this way is practically constant = 1.117. Benzene and its derivatives give a somewhat higher value,  $n_c = 1.160$ . For these two groups of substances, the value of  $(n_c^2 - 1)/(n_c^2 + 2)$ , which represents the fraction of the total volume actually occupied by the molecules at the critical point, is found to be equal to 0.077 and 0.103 respectively. These values are approximately one-third of the corresponding theoretical volume ratios.

In homologous series of aliphatic compounds and in the series of mono-halogen derivatives of benzene, the ratio of the density at the ordinary temperature to the critical density increases with increasing molecular weight. The value of  $(n^2 - 1)/(n^2 + 2)$  shows a similar variation. H. M. D.

**The Dispersion of Ultra-violet Rays by Organic Substances.** VICTOR HENRI (*Compt. rend.*, 1914, 158, 1892—1894).—The author has measured the refractive indices of methyl, ethyl, propyl, butyl, amyl and heptyl alcohols, of glycol and of pentane, hexane, heptane and cyclohexane for rays of wave-length  $\lambda = 4200$ —2150, and from his results has calculated the molecular refractive powers for  $\cdot\text{CH}_2\cdot$ , and  $\text{H}\cdot$  and  $\cdot\text{O}\cdot$  of the hydroxyl group. Up to  $\lambda = 2600$  the refractive power of  $\cdot\text{CH}_2\cdot$  is perfectly additive, as in the visible spectrum, whilst for rays of shorter wave-lengths the additivity is only a first approximation. For the substances examined, the variation of the refractive indices can be accurately represented by the formula (I)  $n^2 = a + b\lambda_0^2/(\lambda^2 - \lambda_0^2)$ , and the molecular refractive power by the formula (II)  $[(n^2 - 1)/(n^2 + 2)]M/d = \alpha + \beta\lambda_0^2/(\lambda^2 - \lambda_0^2)$ . The values calculated from formula (I) and found for methyl, ethyl and propyl alcohols agree closely.

The values of the constants  $\alpha$ ,  $\beta$  and  $\lambda_0$  for formula (II), which hold good from  $\lambda = 6563$  to 2150, are:

	$\alpha$ .	$\beta$ .	$\lambda_0$ .
Methyl alcohol .....	8.0195	5.1182	1063
Ethyl " .....	12.707	7.1784	1239
Propyl " .....	17.112	10.148	1114
Amyl " .....	26.083	6.792	1502
Pentane .....	24.727	11.62	1205
Hexane .....	29.223	25.45	965

W. G.

**The Application of Spectrum Analysis to the Study of Chemical Equilibria.** GUSTAV F. HÜTNER (*Zeitsch. physikal. Chem.*, 1914, 88, 172—190).—The first part of the paper deals theoretic-

ally with the relationships which exist between the changes of the absorption spectrum of a system in equilibrium and the changes in the equilibrium constants of the system. Mathematical relationships are derived for the connexion between the variable components of the absorption spectrum of the system and the number of participating molecules in the reaction, the reaction equation, and the reaction constants. Four types of problems which can be dealt with by this method are indicated. (1) Those in which the reaction constant is known and in which the number of molecules and the reaction equation can be calculated. In cases of this kind, the optical method serves only as a confirmation. (2) Those in which the reaction equation is known and the number of molecules can be calculated. In this case the reaction constant can be deduced by the optical method. (3) Those in which the number of reacting molecules is known; here the reaction equation and constant can be determined by the optical method; and (4) those cases in which nothing is known or calculable; here all three quantities, the reaction constant and equation and the number of molecules reacting, can be determined by the optical method.

The method is applied to the determination of the second and third dissociation constants of purpurin. The measurements consist in photographing the absorption spectrum of solutions of purpurin in pyridine, ammonia solution, normal sodium hydroxide solution, and in an excess of very concentrated sodium hydroxide solution. From the measurements the dissociation constants are calculated to  $2 \times 10^{-11} > k'' > 2 \times 10^{-10}$  and  $1 \times 10^{-15} < k''' < 5 \times 10^{-15}$ . The first and second dissociation constants of alizarin are also determined, and the values  $k' = 4.8 \times 10^{-8}$  and  $k'' = 1.15 \times 10^{-12}$  obtained. By another method (this vol., i, 701) the author has found these values to be  $k' = 5.0 \times 10^{-8}$  and  $k'' = 1.10 \times 10^{-12}$ . From the results obtained by Niggemann (*Diss.*, Leipzig, 1913), the absorption spectra of nitric acid in various states of dilution the author shows that the equilibrium  $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 \cdot \text{H}_2\text{O}$  or  $2\text{HNO}_3 + 2\text{H}_2\text{O} \rightleftharpoons (\text{HNO}_3 \cdot \text{H}_2\text{O})_2$  exists in these solutions. J. F. S.

**Direct Spectrum Analysis by means of the Secondary Rays of Röntgen Rays.** MAURICE DE BROGLIE (*Compt. rend.*, 1914, 158, 1785—1788).—A study of the secondary spectra emitted by substances struck by primary Röntgen rays places the elements in the same position in the periodic classification as is obtained by calculation from Moseley's formula. Elements with an atomic weight of less than 28 have not shown any secondary radiation, whilst with elements of atomic weight between 30 and 50 special precautions are necessary to make the radiations apparent.

W. G.

**Oxygen in the Sun.** K. W. MEISSNER (*Physikal. Zeitsch.*, 1914, 15, 668—670).—The three red lines  $\lambda 7772$ ,  $7774$ , and  $7775$ , which are emitted by the iron arc only at the anode, have been attributed by Runge and Paschen to oxygen (compare *ibid.*, 1913, 14, 1267). According to the author's observations, the oxygen

doublet  $\lambda 8446$  is also observable in the anode spectrum of the arc. Both the triplet and the doublet are shown by the solar spectrum, and an accurate comparison of the wave-lengths has been made for the iron arc and the solar spectra.

The fundamental triplet of the principal and second subordinate series of sulphur has also been found in the anode spectrum in the arc discharge between an iron pyrites anode and an iron cathode. The wave-lengths of these three lines were found to be  $\lambda 9212.80$ ,  $9228.17$ , and  $9237.71$  in terms of the international normals.

H. M. D.

**High-frequency Spectra and the Periodic Table.** W. M. HICKS (*Phil. Mag.*, 1914, [vi], 28, 139—142).—A discussion of the grouping of the elements suggested by Rydberg (compare succeeding abstract) in reference to the high-frequency spectra. Certain modifications of the table given by Rydberg are proposed in accordance with spectroscopic evidence.

H. M. D.

**The Ordinals of the Elements and the High-frequency Spectra.** J. R. RYDBERG (*Phil. Mag.*, 1914, [vi], 28, 144—149).—In a previous paper (*Lunds. Univ. Arsskrift*, 1913, 9, No. 18) the author has suggested that the elements fall naturally into quadratic groups consisting of  $4p^2$  elements ( $p$  being the number of the group). The two short series correspond with  $p=2$ , and give a group of sixteen elements, extending from helium to chlorine. The two recognised long series correspond with  $p=3$ , and give a group of thirty-six elements, extending from argon to iodine. The next group, corresponding with  $p=4$ , is supposed to contain sixty-four elements, and commences with xenon. In this system the elements are characterised by a succession of integral numbers (ordinals) which determine the properties of the various elements.

The fact that Moseley (this vol., ii, 326) has shown the existence of a relation between the "atomic numbers" and the frequencies of the X-ray spectra of the different elements, and that the "atomic numbers" are practically identical with the "ordinals," is supposed to afford strong support for the arrangement of the elements into quadratic groups.

H. M. D.

**Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.** I. (Hon.) R. J. STRUTT (*Proc. Roy. Soc.*, 1914, A, 90, 364—372).—In a previous paper (*A.*, 1913, ii, 279) it was shown that mercury vapour, allowed to distil from the arc, in a vacuum, into a cooled lateral tube, remains luminous for a considerable distance away from the region of discharge. Methods have now been devised which permit of the observation of luminous jets of the vapours of other metals.

As the luminous vapour moves away from the region of the arc discharge, the rate at which the different lines in the spectrum die out is not always the same. In general, the lines belonging to any given series die out at the same rate, but other series of

lines may be extinguished more or less rapidly than the first. In the case of sodium, the lines of the two subordinate series die away at the same rate, but the principal series is extinguished less rapidly. Differences in the duration of the spectral constituents have also been observed with potassium, magnesium, and zinc.

In some cases the luminous jet shows a band spectrum. For the alkali metals, this continuous spectrum lies beyond the limit of the subordinate series.

H. M. D.

**Emission Spectra of the Common Gases.** F. CROZE (*Ann. Physique*, 1914, [ix], 1, 35—134. Compare A., 1912, ii, 613; 1913, ii, 85; 1914, ii, 2).—A detailed account is given of wave-length measurements and of observations on the Zeeman effect in the emission spectra of hydrogen, oxygen, and nitrogen. The apparatus employed was designed so as to facilitate the investigation of the ultra-violet region, and photographic records have been obtained which afford information in regard to the emission spectra up to about  $\lambda$  8000.

A number of new lines and bands have been discovered. These include ninety-eight lines in the second hydrogen spectrum between  $\lambda$  6852 and  $\lambda$  8029, thirty-one lines in the elementary spectrum of oxygen between  $\lambda$  5316 and  $\lambda$  7152, sixteen bands in the first nitrogen group, the least refrangible having the wave-length  $\lambda$  9108, and two bands in the cathodic spectrum of oxygen at  $\lambda$  6853 and  $\lambda$  5007.

The negative bands of oxygen and the most intense bands in the first nitrogen group have been resolved into lines, for which wave-length measurements are recorded. The arrangement of these lines in series is also discussed.

The mode of distribution of the lines in the second hydrogen spectrum, which do not show the Zeeman effect, has been investigated, with the result that the vibration frequencies are found to correspond with eight arithmetic series.

The Zeeman effect has been measured in the first hydrogen spectrum, for the most intense lines in the second spectrum, the whole of the lines in the elementary spectrum of oxygen and all the lines in the first nitrogen spectrum. The bands of the second positive and the negative nitrogen groups, of the "Swan" and the carbon monoxide spectra and of the cyanogen group  $\lambda$  3883, do not exhibit the Zeeman effect. This effect is, however, shown by the resolved bands of the first positive nitrogen group, although the unresolved bands have been previously stated to be unacted on by a magnetic field.

H. M. D.

**The Spectra given by Carbon and some of its Compounds; and, in particular, the "Swan" Spectrum.** W. MARSHALL WATTS (*Phil. Mag.*, 1914, [vi], 28, 117—128).—The views put forward by different observers in explanation of the "Swan" spectrum are summarised, and an account is given of experiments in which the author has observed this spectrum under conditions which seem to preclude the presence of oxygen.

The experiments were made with a spark-discharge apparatus consisting of a rectangular block of transparent fluorspar in which a cylindrical cavity was bored. The lower end of this cavity was closed by a copper electrode ground into the spar. A platinum wire served as the upper electrode, and the discharge vessel was contained in a large glass tube which could be exhausted. Various oxygen-free carbon compounds were distilled over phosphoric oxide into the fluorspar vessel whilst the glass tube was kept exhausted, and the spectrum emitted by the spark discharge within the liquid was observed. Carefully purified materials were employed in all cases. Heptane, hexane, octane, carbon tetrachloride, and chlorobenzene all gave a brilliant "Swan" spectrum. On account of the rapid separation of carbon, only a few seconds were available for observation, and the spectrum could not be photographed.

The numerical relations between the wave-lengths of the lines of the spectrum are discussed, and it is shown that the experimental data may be more accurately represented by the formula  $F = 2407.015 - 19.6(p + 0.00309)^2 + 11.6422(m + 0.834291)^2$ , where  $p = 45, 44, 43$ , and  $m = 63, 64, 65, 66, 67, 68, 69$ , than by Deslandres' formulae.

Special reference is made to the three lines  $\lambda$  4381.93, 4371.31, and 4365.01, which were attributed by Deslandres to hydrocarbons, whereas in the author's opinion there can be little doubt that these three lines form a part of the "Swan" spectrum. H. M. D.

**Influence of Solvents on the Optical Activity of Methyl Hydrogen, ortho- and *allo*-Camphorates, and Normal Camphorate.** J. MINGUIN and R. BLOC (*Compt. rend.*, 1914, 158, 1997—1999).—An extension of the work previously described (compare this vol., ii, 403), a large number of different organic solvents having been used. All solvents containing a benzene nucleus considerably increase the optical activity of the ortho-ester, but have a much less marked effect on the *allo*-ester. The lists obtained by arranging the solvents in the order of increasing optical activity of the ortho- and *allo*-esters, respectively, are quite different. Solvents of the same series with the same functional group have the same influence on the optical activity of either the ortho- or the *allo*-ester, the influence exerted being apparently related to the chemical nature of the solvent. The values obtained for the normal ester are intermediate between those for the ortho- and *allo*-esters, and in some cases are very close to their arithmetic mean. W. G.

**Thermodynamic Consideration of Photochemical Equilibria.** A. SCHMIDT (*Arch. Sci. phys. nat.*, 1914, [iv], 37, 493—511).—A theoretical paper in which the author applies thermodynamic reasoning and Planck's theory of absorption of radiant energy to the discussion of photochemical equilibria. This leads to the view that there are three groups of photochemical reactions. In those which belong to the first group, radiant energy is liberated, and an increase in the frequency of the incident radiation is unfavour-



able to the photochemical change. Those belonging to the second group are endo-energetic, and an increase in the frequency favours the photochemical reaction. In the case of reactions which belong to the third group, the equilibrium is independent of the frequency of the radiation. The action of the light consists simply in increasing the velocity of the opposing reactions, after the manner of a catalyst.

H. M. D.

**Photochemical Decomposition of Hydrogen Peroxide.** II. J. HOWARD MATHEWS and HARRY A. CURTIS (*J. Physical Chem.*, 1914, 18, 521—537. Compare this vol., ii, 255).—Several substances have been added to solutions of hydrogen peroxide, the mixtures submitted to ultra-violet light, and the effect of these substances on the rate of decomposition investigated. The method of investigation is the same as that previously adopted (*loc. cit.*). It is shown that acetamide (0.037%), carbamide (0.05%), boric acid (0.044%), and barium chloride (0.037%) have no action on the rate of decomposition; acetic acid, tartaric acid (0.095%), phosphoric acid (0.152%), sulphuric acid (0.0086%) (0.086%) (0.171%), potassium nitrate (0.031%), potassium chloride (0.023%), and sodium chloride (0.011%) (0.05%) exercise a slight retarding action on the rate of decomposition; benzoic acid, calcium hydroxide (0.002%), sodium hydroxide (0.053%), and barium hydroxide (0.007%) exercise a strong retarding action, and barium nitrate (0.037%) increases the rate of decomposition. The same catalysts do not effect the thermal decomposition and the photolytic decomposition of hydrogen peroxide in the same way. There is no general relationship between the chemical nature of a compound and its catalytic effect on the photolysis of hydrogen peroxide. The magnitude of the catalytic effect and the concentration of the catalyst vary in the same direction, but there is no direct proportionality between the two. Neither the change in the light absorption nor the change in the surface tension of a hydrogen peroxide solution, brought about by the addition of a small amount of a catalyst, seems adequate to explain the marked catalytic effect produced.

J. F. S.

**The Different Methods of Photolysis of Oxalic Acid by Ultra-violet Rays of Different Wave-lengths.** DANIEL BERTHELOT (*Compt. rend.*, 1914, 158, 1791—1793. Compare A., 1911, ii, 170; 1913, ii, 819).—The photolysis of oxalic acid consists in a primary decomposition into carbon dioxide and formic acid, followed by a secondary decomposition of the formic acid in the nascent state, the products of the secondary reaction being carbon monoxide and water for rays of long wave-length and carbon dioxide and water for waves of short wave-length.

W. G.

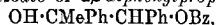
**Chemical Action of Light.** XXX. GIACOMO CIAMICIAN and P. SILBER (*Ber.*, 1914, 47, 1806—1814; *Atti R. Accad. Lincei*, 1914, [v], 23, i, 859—867).—Many of the photochemical reactions previously

described are confirmed, and the results recently communicated by Paternò and others (this vol., ii, 234) are criticised.

Benzaldehyde and benzophenone give the compound  $C_{27}H_{22}O_3$ , m. p.  $245^\circ$  (A., 1911, i, 647), and not a trimeric benzaldehyde (Paternò).

Whereas acetone and ethyl alcohol yield, among other substances,  $\beta$ -methylbutylene  $\beta$ -glycol (A., 1911, i, 513), acetophenone is only changed into the isomeric pinacones (compare A., 1901, i, 330). No combination takes place between benzophenone or acetophenone and isopropyl alcohol, the pinacones and acetone being the products. Phenyl ethyl ketone does not react with alcohol like methyl ethyl ketone (A., 1912, i, 537); the transformation of the ketone is not complete after some months, and the products can only be separated with difficulty into the isomeric *phenyl-ethylpinacones*,  $C_{18}H_{22}O_2$ , leaflets, m. p.  $138-139^\circ$ , and large, well-developed crystals, m. p.  $113^\circ$ , respectively.

It was previously found that benzophenone and benzyl alcohol gave hydrobenzoin, benzopinacone, and also triphenylethylene glycol (A., 1903, i, 562). Paternò exposed a mixture of acetophenone and benzyl alcohol to light, but the only product which he described was  $\alpha\beta$ -diphenylpropanediol. The authors had also left such a mixture for some months, and now describe the examination of the product. After removing the unchanged reagents by steam, the residue was extracted with a mixture of much light petroleum with a little benzene. The extract deposited acetophenonepinacone, and the syrup which remained on evaporation of the mother liquor was benzoylated. The product was crystallised from much alcohol, which deposited dibenzoylhydrobenzoin, leaving the *monobenzoate* of  $\alpha\beta$ -diphenylpropanediol,



in solution. The latter was isolated in white needles, m. p.  $147-148^\circ$ , but the *monobenzoate* obtained directly from Tiffeneau and Dorencourt's  $\alpha\beta$ -diphenylpropanediol (*Ann. Chim. Phys.*, 1909, [viii], 16, 252) had m. p.  $139-140^\circ$ , and may therefore be an isomeride.

Paternò also illuminated a mixture of acetaldehyde and alcohol, and believed that he had obtained thereby butane- $\beta$ -diol. The authors had already found this glycol in the case of alcohol and acetone, and had expressed the opinion that its formation was due to a reaction between alcohol and acetaldehyde, the latter being formed during the experiment (A., 1911, i, 514).

The products obtained when methyl ethyl ketone and dilute hydrocyanic acid are exposed to sunlight are quite analogous to the products obtained from acetone (A., 1905, i, 414). In this case, however, the reaction also proceeds in the dark. Ammonium oxalate and oxamide were isolated, but the chief product was

3-methyl-3-ethylhydantoin,  $\begin{matrix} CMeEt \cdot NH \\ CO-NH \end{matrix} > CO$ , which formed large,

colourless prisms, m. p.  $146^\circ$ , and was hydrolysed by hydrochloric acid in a sealed tube to  $\alpha$ -amino- $\alpha$ -methylbutyric acid (Slimmer,

A., 1902, i, 206). The amino-acid itself was not found among the products. In addition,  $\alpha$ -hydroxy- $\alpha$ -methylbutyramide,  $C_5H_{11}O_2N$ , m. p.  $160^\circ$ , was isolated and hydrolysed by baryta to the acid.

J. C. W.

**Oxidations with Bromine under the Influence of Light.** R. CIUSA and A. PIERGALLINI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 821—825).—When a mixture of lactic acid and bromine water is exposed to light for a day, pyruvic acid is formed. Tartaric acid in similar circumstances yields formylglyoxylic acid. Mandelic acid yields benzoic acid, benzaldehyde, and phenylglyoxylic acid. In the dark the same products are obtained, but benzoic acid is produced only in small quantity. Glycerol is oxidised to glycerose by bromine water when exposed to light. Mannitol in similar circumstances yields mannose. Citric acid yields pentabromoacetone. In all cases, except that of mandelic acid mentioned above, control experiments carried out in the dark gave either no oxidation products at all or only traces of them.

R. V. S.

**The Transformation of Radiant Energy into Chemical Energy.** S. C. LIND (*Le Radium*, 1914, 11, 108—111).—The author has shown by the study of eight reactions in gases and three in liquids that the number  $N$  of pairs of ions produced under the influence of  $\alpha$ -rays is approximately equal to the number  $M$  of molecules entering into the reactions brought about by the rays. In the electric discharge in gases the chemical action is frequently a thousand times greater than would be the case if this application of Faraday's law were followed, which is to be explained on the view that the great proportion of ions produced by collision recombine and produce their chemical effect before reaching the electrodes. The hypothesis of Warburg on the calculation of the quantity of ozone produced by the  $\alpha$ - and  $\beta$ -rays of radium is discussed, and shown to lead to a value too low on this account. From the ratio  $N/M$  found previously for several endothermic gaseous reactions, the proportion of the radiant energy converted into chemical energy is calculated to be of the same order—about 2%—as has been found in other chemical reactions effected by radiant energy. In exothermic reactions the proportion is of the same order, but reaches 10% in the case of the decomposition of water. The velocity of the reactions obeys the uni-molecular law, not because they are uni-molecular, but because the absorption of radiant energy is proportional to the concentration in the gaseous system. It is suggested that the ions play the part of intermediaries in the chemical reactions.

F. S.

**The Ultimate Rays of Elements in Different Luminous Sources.** ARNAUD DE GRAMONT (*Compt. rend.*, 1914, 159, 5—12).—A critical *résumé* of the author's work and that of other observers on this subject (compare A., 1907, ii, 517; 1908, ii, 645; 1910, ii, 85, 811; 1912, ii, 875; Hartley and Moss, A., 1912, ii, 821; Runge and Precht, A., 1903, ii, 346, 621; 1904, ii, 461), in which the

author deduces the following rules: (1) If, in sources of different temperatures the rays of an element do not maintain the same sensibility, the ultimate rays will, in every case, consist of a very small number of lines of great sensibility in the condensed spark. (2) The rays of maximum sensibility will be less refrangible as the temperature of the luminous source is lower. W. G.

**The Coefficient of Diffusion of X-Rays by Substances with Slight Atomic Weights (Organic Substances in particular).** H. GUILLEMINOT (*Compt. rend.*, 1914, 159, 56—59).—The author has deduced a formula for calculating the secondary radiation emitted by the emergent face of a paraffin filter, knowing the intensity of the initial ray and the thickness of the filter, and has tested its validity in the case of the paraffin filter and also for Argon. W. G.

**The Passage of  $\alpha$ -Particles through Photographic Films.** H. P. WALMSLEY and W. MAKOWER (*Proc. Physical Soc., London*, 1914, 26, 261—263).—A flat metal plate was exposed to a fraction of a millicurie of radium emanation for a few seconds, and laid on an Ilford process plate. The darkening of the plate, due to the  $\alpha$ -rays of radium-A, was just visible to the naked eye after development, and was examined under the microscope and microphotographs taken. These showed the tracks of the single  $\alpha$ -particles through the film, with many of the characteristics demonstrated by C. T. R. Wilson's cloud photographs. The method is exceedingly simple, and lends itself to the study of the scattering of  $\alpha$ -particles by heavy atoms such as silver. Plates are reproduced, at a magnification up to 1800 diameters, showing the single darkened haloid grains in the track of the  $\alpha$ -ray. F. S.

**Fitful Point Discharges and the Electric Method of Counting  $\alpha$ -Particles.** H. GEIGER (*Ann. Physik*, 1914, [iv], 44, 813—815. Compare this vol., ii, 236).—Polemical. The results obtained by Myssovski and Nesturch are in part to be explained by secondary  $\beta$ -rays generated from the walls of the chamber under the action of the  $\gamma$ -rays. That the discharges in question are caused by individual  $\alpha$ -particles, and not by natural disturbances, is proved by sending the  $\alpha$ -particles through two counting chambers placed one behind the other, when, almost without exception, the discharges take place simultaneously in the two chambers. The criticism shows that the right experimental conditions for counting the  $\alpha$ -particles were not realised. F. S.

**Absorption and Reflexion of  $\beta$ -Particles Measured by Direct Counting.** ALOIS F. KOVARIK and LOUIS W. MCKEEHAN (*Physikal. Zeitsch.*, 1914, 15, 434—440).—Using Geiger's method for the direct counting of  $\beta$ -particles, by the fitful discharges from a sharp point kept at high potential, the number of  $\beta$ -particles reflected and transmitted through various substances was determined. The number transmitted of the  $\beta$ -particles of radium-B

and the active deposit of thorium, respectively, did not follow an exponential law with increasing thickness of matter, although the ionisation follows this law in these cases. The fraction of the whole number transmitted in each similar layer usually becomes less instead of remaining constant. The reflected and transmitted rays are more strongly absorbed than the initial rays. The number reflected by different elements of increasing atomic weight increases in the same way as the ionisation due to the reflected rays, which shows that the loss of velocity of the rays by reflexion is nearly independent of the nature of the reflecting material. Very thin foils increase the number of  $\beta$ -particles, and in certain circumstances the direction of the new  $\beta$ -particles generated is nearly normal to that of the thin foil. F. S.

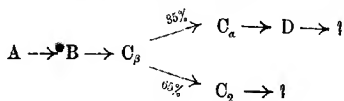
**Disintegration of Radium Emanation in a Helium Atmosphere.** W. MARCKWALD (*Physikal. Zeitsch.*, 1914, 15, 440—441).—No difference in the normal rate of disintegration of the radium emanation was observed when the emanation was allowed to decay in an atmosphere of helium, such as might have been expected to occur were the reaction at all reversible. F. S.

**The Electrochemical Properties of Radium-B and Thorium-B.** Z. KLEMENSIEWICZ (*Compt. rend.*, 1914, 158, 1889—1891).—In an endeavour to find some method of distinguishing between the isotopic elements lead, radium-B, and thorium-B, the author has proceeded as follows. An amalgam of lead (1 gram of lead in 5—10 c.c. of mercury) was shaken for several minutes with 5 c.c. of  $N/10$ -lead nitrate solution, acidified with  $N/50$ -nitric acid, which had been in contact with 0.1 curie of radium emanation for several hours, and then boiled. After the shaking, the amalgam was removed and washed with a solution of  $N/10$ -mercurous nitrate and  $N$ -nitric acid. This and the original solution were then evaporated to dryness with hydrochloric acid and heated at  $125^{\circ}$  for fifteen minutes, leaving two fractions of lead chloride crystals. In order to remove any radium-C, the two fractions were dissolved in warm  $N/100$ -nitric acid, and a plate of nickel plunged into each solution. The solutions were then evaporated to dryness again with hydrochloric acid, and the crystals powdered and spread on two equal brass disks. The total radiation was then measured by means of a quartz piezo-electrometer. Similar measurements were made with thorium-B. In neither case was there any difference in activity between the two fractions of crystals, thus proving that the electrolytic potentials of radium-B and thorium-B are equal to those of lead, the differences observed being much less than those which are obtained with specimens of the same metal which have undergone different mechanical treatment. W. G.

**Volatility of Thorium Active Deposit.** T. BARNATT and A. B. WOOD (*Proc. Physical Soc., London*, 1914, 26, 248—260).—The thorium active deposit, on platinum or quartz plates, was heated in an electric furnace, usually for fifteen minutes, to

accurately known temperatures, and the percentage of thorium-*B* and of thorium-*C* respectively volatilised was determined by examination of the decay curves prior to and after heating. The  $\alpha$ -ray measurements showed that both the *B*- and *C*-members begin to volatilise at 750°, and volatilisation is complete at 1200°, but at intermediate temperatures a greater proportion of the *B*- than of the *C*-member is volatilised. There is an inflexion on the curve showing the proportion of the *C*-member volatilised, at a point where about 35% of the  $\alpha$ -ray activity has been removed and at about 900°. The  $\beta$ -ray curves, on the other hand, showed that the *C*-member does not begin to volatilise until 900°. With films deposited from solutions of the active deposit in strong acids volatilisation occurred at the same temperatures as stated for the nitric acid solution, but for a hydrochloric acid solution volatilisation commences at 300°. Thorium-*D* was found to begin volatilising at 500° in the case of a film not dissolved in acid.

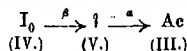
In order to explain the results, a new member of the disintegration series is assumed to exist, according to the following scheme:



in which branching occurs at the member  $C_{\beta}$ , which has a half-period of 60.3 minutes, and gives  $\beta$ -rays. In the minor branch the product is supposed to be a new member,  $C_{\alpha}$ , of period one minute or less, giving the  $\alpha$ -rays of range 5.0 cm.  $C_{\beta}$  is volatile at 900°, and  $C_{\alpha}$  at 750°. The product  $C_2$  of the above scheme (often called *C'*) is that which gives the  $\alpha$ -rays of 8.6 cm. range, and is usually supposed to have a period of  $10^{-11}$  second. This scheme agrees with the facts better than any other that can be devised. The range of the  $\alpha$ -rays of  $C_{\alpha}$  corresponds, by the Geiger-Nuttall relation, with a period of one minute or less. F. S.

**The Magnetic Spectrum of the  $\beta$ -Rays of Uranium-X.** O. VON BAERER, O. HAHN, and L. MEITNER (*Physikal. Zeitsch.*, 1914, 15, 649—650).—The magnetic spectrum of the more penetrating  $\beta$ -rays of uranium-X consists of a broad, indistinct band which affords evidence of intensity maxima at velocities corresponding with 0.96 and 0.82 of the velocity of light. The less penetrating rays give rise to a shallow band at the velocity ratio 0.59, and to two sharp lines at 0.52 (weak) and 0.48 (strong). An attempt to resolve the spectrum of the high-speed rays into lines gave a negative result with the comparatively weak preparations of uranium-X which were available for the experiments. Since the  $\gamma$ -radiation of uranium-X is very weak in comparison with the  $\beta$ -radiation, the continuous character of the magnetic spectrum would appear to be in agreement with Rutherford's theory, according to which the emission of  $\gamma$ -rays is connected with the discontinuous character of the  $\beta$ -ray spectrum. H. M. D.

**The Origin of Actinium.** C. GÖHRING (*Physical. Zeitsch.*, 1914, 15, 642—645).—A strong ionium preparation, four years old, was examined for the presence of an "eka tantalum," acting as the parent of actinium, according to the scheme:



by precipitating tantalic acid in the solution. The product was very active, but by repeated solution of the tantalic acid by fusion with potassium hydroxide, and reprecipitation by acid, the activity was removed. It was probably due to ionium. A search for the parent of actinium in pitchblende was made by precipitating tantalic acid in the solution and purifying as above. The product was again practically inactive. Lastly, the uranium-Y separated from 1500 grams of uranyl nitrate was examined for a residual activity, and none was found. It is possible that the method of purification of the tantalic acid adopted may have separated the substance sought.

F. S.

**The Distribution of the Radio-elements in Rocks. I. Monazite Sand.** M. BALTOCH and G. WEISSENBARGER (*Zeitsch. anorg. Chem.*, 1914, 88, 88—102).—The separation of the minerals in monazite sand may be effected magnetically, magnetite being first removed, then ilmenite, by using an electromagnet, and then monazite, by using a strong field. Zircon is then separated from quartz and felspar in a centrifugal apparatus. The quartz and felspar can only be imperfectly separated by using heavy liquids.

Brazilian monazite sand is thus found to contain 75% monazite, 12.4% ilmenite, 8.8% zircon, about 3% quartz, and the remainder magnetite and felspar.

The other minerals are freed from any adhering traces of monazite by treatment with hot concentrated sulphuric acid. Zircon is found to be coloured violet, as if by the action of radium, and this coloration is not removed by the acid treatment. The quartz is not coloured.

The quantities of radium and thorium have been determined by electrometric measurements, with the exception of the thorium in monazite, which is estimated analytically. The following values for the ratio Th:Ra are found: monazite,  $3.10 \times 10^8$ ; zircon,  $1.51 \times 10^6$ ; magnetite,  $1.49 \times 10^8$ ; ilmenite,  $1.10 \times 10^7$ ; felspar,  $1.94 \times 10^6$ ; quartz,  $2.13 \times 10^6$ , the total quantity in the last two minerals being very small. Uranium is present in monazite in sufficient quantity to be recognised chemically. Two analyses give 0.062 and 0.065% U, the ratio Ra:U being thus  $3.22 \times 10^{-7}$ . The mesothorium preparations from the sand contain 0.25% mesothorium, 25.00% radium, and 74.75% barium, and it is not possible to alter the ratio in any considerable degree by separating the component minerals.

C. H. D.

**Radioactivity of the Rocks of the Kolar Gold-fields.** HERBERT EDMESTON WATSON and GOSTABEHARI PAL (*Phil. Mag.*, 1914, [vi], 28, 44—51).—A modification of Joly's fusion method of

estimating radium in rocks by means of the emanation liberated is described, in which 10 grams of the powdered rock are heated with 2 grams of sodium carbonate and 50 grams of unfused stick potassium hydroxide in a copper flask, previously exhausted by a Fleuss pump. The rocks of the Kolar gold-fields in Mysore, 80 kilometres east of Bangalore, and extending to a depth of 1·2 kilometres, were found to contain only very minute quantities of radium. A source of error was found in the hydrogen liberated in the reaction, which causes the leak produced by a given quantity of radium emanation to be considerably reduced. It was necessary to pass the gas through heated copper oxide before introducing it into the electroscope. The mean amount of radium in the gold-bearing schists was  $0\cdot19 \times 10^{-12}$  gram per gram of rock, and was approximately the same throughout the whole of the workings, independently of the depth. The temperature gradient in the Kolar mines is quite abnormally small, just as the radium content of the rock is extraordinarily low. Other specimens of different rocks of later geological age from the same locality gave amounts of radium varying from 0·8 to 6·9 ( $\times 10^{-12}$  gram per gram).

F. S.

**Radioactivity of the Waters of Saratoga Springs, New York.** RICHARD B. MOORE and C. F. WHITEMORE (*J. Ind. Eng. Chem.*, 1914, 6, 552—553).—The total activity of these waters, with one exception, was found to be low. A large proportion of the activity is due to the presence of dissolved radium salts. Many of the springs contain barium hydrogen carbonate, and, to some extent, there is a relation between the quantity of radium and that of this salt. A connexion could not be traced between the activities and the quantities of the other salts in solution.

W. P. S.

**Analysis of Radioactive Substances by Sublimation.** C. RAMSAUER (*La Radium*, 1914, 11, 100—107).—An apparatus is described, consisting of a surface of platinum foil, electrically heated, inside a closed desiccator attached to a rubber balloon to allow for the expansion of the gas. Above the heated surface is a tray containing ice, and charged negatively to 220 volts. Radioactive substances are heated on the foil, and the active deposit products, sublimed on the cold surface, are employed to determine the relative proportions of radium, thorium, and actinium present. The heating is maintained for four minutes at 1150°, and measurements of the decay curves are started five minutes from the commencement of heating. The theoretical curves for the pure substances are calculated, and the experimental curves are shown to agree. An analysis by this method of the thermal sediment of Kreuznach gave 1·75 mg. of radium per 1000 kilos., in good accord with the result of the emanation method, 1·84 mg. per 1000 kilos. The amounts of thorium-X and actinium-X present were also estimated.

F. S.



**Distribution of Solvents between Solutes. III. Electrical Conductivity of Mixtures of Salts in Organic and Mixed Solvents.** A. G. DOROSCHEVSKI and S. V. DYORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 453—459. Compare this vol., ii, 419).—The fact that the conductivities of mixtures of potassium and tetraethylammonium iodides in water, methyl or ethyl alcohol, methyl ethyl ketone, acetonitrile and nitromethane, are in agreement with Barmwater's formula (compare Philip and Courtman, *T.*, 1910, 97, 1261), in conjunction with the authors' conclusions (*A.*, 1913, ii, 1014), indicates that solutions of the two above iodides in all these solvents are isohydric at equivalent concentrations. This is, indeed, found to be the case, as nearly as can be expected in view of the difficulties attending measurement of the conductivity in the solvents employed.

Deviations from this rule might be expected with feeble electrolytes and with solvents exhibiting strongly marked chemical functions and slight ionising capacity. The authors have investigated the conductivities of sodium and potassium iodides and their mixtures in water and in absolute methyl and ethyl alcohols. In absolute methyl alcohol,  $\lambda_{84}$  has the values 74.92 and 80.30 respectively for sodium and potassium iodides, and in absolute ethyl alcohol 28.73 and 29.50. With mixtures of the iodides, the results obtained are analogous to those of Philip and Courtman.

Further measurements of the conductivity were made on sodium and potassium chlorides and their mixtures, and on barium chloride and nitrate and their mixtures, in aqueous ethyl alcohols of different strengths. The results obtained lead to the conclusion that strong electrolytes in organic and mixed solvents form solutions which are isohydric at equivalent concentrations.

T. H. P.

**Dielectric Constant of Gases.** L. VERAÏN (*Ann. Physique*, 1914, [ix], 1, 255—296, 523—590).—Measurements have been made of the dielectric constants of air, carbon dioxide, and sulphur dioxide by a method involving the comparison of the capacity of a condenser containing the gas under examination as dielectric with that of a standard condenser. The influence of temperature was determined by measurements between 0° and 70°, and the pressure was varied from about 1 to 6.5 atmospheres for air and carbon dioxide, and up to 2.4 atmospheres for sulphur dioxide.

The results obtained for air are in excellent accord with the requirements of Maxwell's relation  $K = n^2$ , where  $K$  is the dielectric constant and  $n$  the refractive index. For the other two gases, the agreement is much less satisfactory.

The Mossotti-Clausius relation  $(K-1)/(K+2)d = \text{constant}$ , which for gases at low pressures may be written in the form  $(K-1)/d = \text{constant}$ , is satisfied by the data for air and carbon dioxide within the limits of experimental error, but a much greater divergence is shown by the numbers for sulphur dioxide.

Measurements were also made of the dielectric constant of liquid carbon dioxide and of its saturated vapour at temperatures

between  $-4^{\circ}$  and the critical temperature ( $31.4^{\circ}$ ). In this case Drude's method was employed. If the values of the dielectric constant are plotted as a function of the temperature, an apparently continuous curve is obtained, the tangent at the critical temperature being perpendicular to the temperature axis.

H. M. D.

**The Thermoelectric Force of Tin Selenides.** H. PÉLABON (*Compt. rend.*, 1914, 158, 1897—1900. Compare this vol., ii, 521).—The author has determined the thermoelectric force of couples consisting of platinum with tin-selenium alloys of varying composition at various temperatures, and has plotted the curves, showing the relationship between the thermoelectric force and the percentages of tin and selenium in the alloys. The form of the curves varies with the temperature, but all show an angular point corresponding with the selenide  $\text{SnSe}$ . The selenide  $\text{SnSe}_2$  is not indicated by any particular change in direction of the curve. At the hot juncture the current passes from platinum to the alloy for  $\text{Pt-SnSe}$ , and from the alloy to platinum for  $\text{Pt-SnSe}_2$ . A couple formed by platinum and an alloy of composition intermediate between that of the two selenides, and varying slightly with the temperature, will have no thermoelectric force. W. G.

**Application of the Theory of Allotropy to Electromotive Equilibria.** A. SMITS and A. H. W. AREN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 37—54. Compare this vol., ii, 165).—If the equilibrium at the surface of contact between a metal and a solution of one of its salts is disturbed by anodic dissolution or cathodic deposition, a difference of potential will be set up between the electrode and a "normal" auxiliary electrode. For very small current densities, the external equilibrium will not, in general, be sensibly disturbed, but as the current density increases, it is to be expected that the departure from the normal condition of equilibrium will become evident, and that the resulting difference of potential between the electrode and the auxiliary electrode will increase. If the internal equilibrium is set up very quickly, the potential difference in question will be very small, but much larger values are to be expected if the adjustment of the internal equilibrium is comparatively slow.

Experiments have been made in which currents of varying intensity were passed between rods of silver, copper, lead, nickel, cadmium, bismuth, iron, and aluminium, immersed in solutions of the corresponding salts, and in which the anodic and cathodic polarisation was determined by the aid of an auxiliary electrode of the same metal.

The results obtained lead the author to the conclusion that the internal equilibrium is very quickly set up in silver, copper, and lead, very slowly in nickel, and at an intermediate rate in cadmium. The behaviour of bismuth, iron, and aluminium suggests that catalytic agencies play a considerable part in connexion with the polarisation phenomena.

H. M. D.

**Stability and Oxidation Potential of Hypochlorites.** Contributions to Catalysis and a Hypochlorite-Carbon Cell. K. A. HOFMANN and KURT RITTER (*Ber.*, 1914, 47, 2233-2244).—The authors have compared the behaviour of calcium hypochlorite, free from chloride, with that of bleaching powder and of a mixture of calcium hypochlorite and calcium chloride towards various reagents (compare Taylor, T., 1910, 97, 2541). Towards carbon dioxide-free, dry air, calcium hypochlorite and bleaching powder show very little difference in behaviour at 90°, there being only a very slight loss of chlorine in both cases. When exposed to moist air containing carbon dioxide at the ordinary temperature, the bleaching powder loses a greater proportion of its available chlorine than does the calcium hypochlorite; a mixture of calcium hypochlorite and calcium chloride behaves similarly to the bleaching powder. In an atmosphere of dry carbon dioxide, calcium hypochlorite loses a small percentage of its available chlorine after five hours' exposure; the mixture of hypochlorite and chloride loses a slightly greater percentage, whilst the bleaching powder loses all its available chlorine. In a current of moist carbon dioxide, both calcium hypochlorite and bleaching powder lose all their active chlorine, but whilst the latter evolves only chlorine, the former evolves both chlorine and hypochlorous acid; a mixture of hypochlorite and chloride behaves similarly to bleaching powder. In a solution of calcium hypochlorite a stream of carbon dioxide gives the ratio: free chlorine:chloride chlorine:chlorate chlorine = 2:1:1, the hypochlorous acid formed in solution decomposing in accordance with the equation  $4\text{HOCl} = \text{HClO}_3 + \text{HCl} + \text{Cl}_2 + \text{H}_2\text{O}$ . In a solution of bleaching powder the free chlorine is increased at the expense of the chlorate chlorine, the ratio being 3:1. Both calcium hypochlorite and bleaching powder behave in the same way towards ammonia, there being an almost quantitative evolution of nitrogen.

Solutions of calcium hypochlorite and of bleaching powder are decomposed catalytically to the same extent by cobalt, nickel, and iridium oxides, whereas the oxides of chromium, iron, manganese, uranium, bismuth, palladium, osmium, thallium, and vanadium are inactive. Calcium hypochlorite solutions are more stable towards ruthenium and rhodium salts, whereas bleaching powder solutions are more stable towards copper sulphate and lead nitrate.

It has been supposed that the oxidising power of hypochlorites and other oxidising agents can be increased by the addition of oxygen-evolving catalysts. Experiments with solutions of sodium hypochlorite and hydrogen peroxide show that this is not the case; oxygen-evolving catalysts, such as iridium powder and cobaltic oxide, simply evolve their oxygen without exerting any appreciable oxidising effect on any oxidisable substances present, for example, anthracene, whereas oxygen carriers, such as osmium tetroxide, increase the oxidising power, that is, raise the oxidation potential of the hypochlorite or hydrogen peroxide. This result can be predicted from thermochemical considerations.

Measurement of the oxidation potentials of solutions of calcium

hypochlorite and of bleaching powder, each saturated with calcium hydroxide, using platinum, magnetite, or gold electrodes, showed they are approximately the same; the potential depends very little on the dilution, but is affected by the alkalinity of the solutions. The bleaching-powder solutions are, however, too unstable for use.

Of various cells which were built up in order to make use of the oxidising powers of hypochlorites, the following gave the highest *E.M.F.*, namely, 2.24 volts, corresponding with a 92.2% yield on the used oxygen: Platinum-sodium hypochlorite solution made alkaline with sodium carbonate | 20% solution of sodium chloride | 10% sodium hydroxide, zinc oxide, zinc.

It was found possible to construct cells with carbon electrodes. Thus the cell: Platinum-sodium hypochlorite, sodium carbonate solution | 2*N*-sodium hydroxide | 2*N*-sodium hydroxide, beechwood charcoal in platinum wire gauze, gave an initial voltage of 0.76–0.91 volt. Quantitative measurements showed that the current yield from this cell was 76% of the oxygen used from the hypochlorite. With a somewhat similar cell it was shown that the electromotively active oxygen was almost completely transformed into carbon dioxide.

It follows that with alkaline hypochlorite solutions at unattackable electrodes a sufficiently strong oxidation potential is obtained to oxidise boxwood charcoal, opposed to it in a galvanic cell; also, from such a cell current may be taken continuously. Before these results are of practical value, however, further investigations are necessary.

T. S. P.

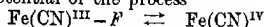
#### The Potential of the Ferricyanide-Ferrocyanide Electrode.

ERICH MÜLLER (*Zeitsch. physikal. Chem.*, 1914, 88, 46–56).—The potential of a number of mixtures of potassium ferrocyanide and potassium ferricyanide in the presence of potassium hydroxide, hydrochloric acid, and potassium chloride has been determined at 0°. The electrode used was either of gold or platinised platinum. The results obtained have been compared with those of Lewis and Sargent (*A.*, 1909, ii, 369) and Fredenhagen (*A.*, 1902, ii, 238). It is shown that the figure which has hitherto been regarded as the potential of the ferrocyanide-ferricyanide electrode is an undetermined and indefinite quantity, which depends not only on the ratio of the concentration of the two salts, but also on the concentrations of the salts themselves. In the presence of *N*-potassium chloride the potential at 0° is expressed by

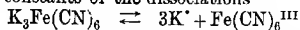
$$e = 0.232 + 0.0546T \log i/o \text{ volts (against } NE),$$

where *i* and *o* are the total concentrations of the ferricyanide and ferrocyanide respectively, and *NE* represents the normal electrode.

The electrolytic potential of the process



is at 0° approximately 0.14 volt (against *NE*), and the ratio of the dissociation constants of the dissociations



and  $\text{K}_4\text{Fe(CN)}_6 \rightleftharpoons 4\text{K}' + \text{Fe(CN)}_6^{IV}$  is approximately 68. The influence of potassium hydroxide and acids on the potential of the

$\text{Fe}(\text{CN})_6^{\text{III}}/\text{Fe}(\text{CN})_6^{\text{IV}}$  electrode is due to a shifting of the dissociation ratio. At small concentrations of potassium ferri- and ferrocyanides, the dependence of the potential on the concentration of potassium hydroxide and potassium chloride at  $0^\circ$  is given by the equation  $\epsilon = 0.24 + 0.0546T \log i/o \cdot \text{K}'$  volts (against  $NE$ ), and on the concentration of free acid by the equation

$$\epsilon = 0.45 + 0.0546T \log i/o \cdot \text{H}' \text{ (against } NE),$$

where  $\text{K}'$  and  $\text{H}'$  respectively are the concentrations of the potassium and hydrogen ions.

J. F. S.

**Electromotive Behaviour of Soluble Sulphides.** ROGER C. WELLS (*J. Physical Chem.*, 1914, 18, 510—520).—The single potentials of acid solutions of hydrogen sulphide and of solutions of sodium hydrogen sulphide, sodium sulphide, and sodium polysulphides have been measured against a calomel electrode. It is shown that solutions of polysulphides behave electromotively in the same way as other oxidation and reduction elements. It is generally impossible to represent their behaviour mathematically without assuming that several polysulphides are present in a rather complicated equilibrium. For mixtures which contain sufficient sulphur to form  $\text{Na}_2\text{S}_2$  and  $\text{Na}_2\text{S}_3$  the normal electrode potential can be obtained by calculation from the relative concentrations of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_4$  by means of the equation

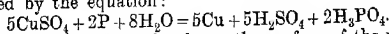
$$E = E_0 - 0.059/6 \log (S^{--})^4/(S_4^{--}),$$

when the value of  $E_0$  is found to be  $-0.208$  volts. On reaching a sulphur concentration corresponding with  $\text{Na}_2\text{S}_4$  there is a sudden shift in the  $E_0$  value which points to a higher polysulphide. On the other hand, solutions which are easily saturated with sulphur have as the expression for their potential the equation:

$$E = -0.26 - 0.029 \log (S^{--}).$$

J. F. S.

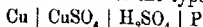
**Positive Ions from Non-metallic Elements. I. Precipitation of Metals from Solutions of their Salts by Yellow Phosphorus.** R. M. BIND and S. H. DIGGS (*J. Amer. Chem. Soc.*, 1914, 36, 1382—1392).—The products obtained by the action of yellow phosphorus on aqueous solutions of copper sulphate are copper and phosphoric acid, together with smaller quantities of copper phosphide and phosphorous acid. The metallic copper was deposited in the form of tubes surrounding the sticks of phosphorus, each tube being covered on the inside with a layer of black copper phosphide. It is probable that the phosphide is formed by the subsequent action of the precipitated copper on the phosphorus and that the phosphorous acid is due to the interaction of the phosphorus and the phosphoric acid formed in the principal reaction. The quantitative measurements indicate that approximately five atoms of copper are precipitated by two atoms of phosphorus, a represented by the equation:



Since the copper is formed only on the surface of the phosphorus or on the surface of conductors connected with the phosphorus, it

probable that the action is electrolytic in character, as represented by the equations:  $5\text{Cu}'' + 2\text{P} = 5\text{Cu} + 2\text{P}''''$ ;  
 $2\text{P}'''' + 10\text{OH}' = 2\text{H}_3\text{PO}_4 + 2\text{H}_2\text{O}$ .

According to this, the primary action consists in the transfer of positive charges from the copper to the phosphorus. In support of this view, it is found that a cell of the type

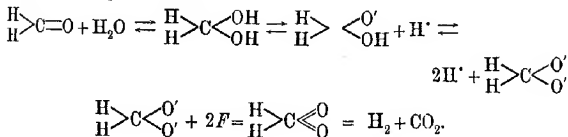


yields a current which passes from the phosphorus to the copper through the solutions. The *E.M.F.* of the cell is about 0.35 volt, and little or no difference is found by varying the concentration of the sulphuric acid solution or by replacing this by distilled water, or by solutions of sodium and magnesium sulphate.

According to these experiments there is no essential difference between the metallic and non-metallic elements in respect of their tendency to form positive ions.

H. M. D.

**Evolution of Hydrogen at the Anode during the Electrolysis of Methyl Alcohol and Formaldehyde.** ERICH MÜLLER and FRIEDRICH HOCHSTETTER (*Zeitsch. Elektrochem.*, 1914, 20, 367—369).—Equal volumes of 4*N*-sodium hydroxide and methyl alcohol were electrolysed in a divided cell using a platinum anode and a current density of 0.1 ampere per 15 sq. cm. The anode products were formic acid and formaldehyde and 135 c.c. of a gas consisting of 97.4%  $\text{H}_2$ , 1.2%  $\text{O}_2$ , and 1.4%  $\text{CO}$ . The amount of gas produced increased as the electrolysis proceeded. The substitution of formaldehyde or formic acid for the methyl alcohol gave no gas evolution at the anode. On substituting a copper anode for the platinum gas, evolution did not take place with methyl alcohol or formic acid, but with formaldehyde pure hydrogen was evolved at the anode, and in amounts equal to that at the cathode. It is shown that in this case the total current can be used in effecting the reaction  $\text{H}_2 = \text{C} = \text{O} + \text{O}'' + 2\text{F}' = \text{H}_2 + \text{CO}_2$ , and this reaction probably consists in the discharge of the ion  $\text{H}_2\text{C}_2\text{O}_2''$ , since formaldehyde behaves as a dibasic acid in alkaline solution. The whole change is represented by the scheme:



J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation.** III. Attempts to Prepare Zirconium, Aluminium, Antimony and Chromium Bronzes. R. KREMAN, JOSEF LORBER, and RUDOLF MAAS (*Monatsh.*, 1914, 35, 581—602. Compare this vol. ii, 96, 422).—Attempts to deposit zirconium electrolytically from (1) an alkaline solution of zirconium hydroxide and tartaric acid, with platinum electrodes,

(2) with a mercury cathode, and (3) from an alkaline solution of zirconium oxychloride and tartaric acid to which a small quantity of an iron salt had been added, all led to negative results; in the last case iron was deposited in the passive condition. Attempts to deposit zirconium along with tin, zinc, and copper respectively from mixed alkaline solutions also failed to give a deposition of zirconium. The deposition of copper from aluminium solutions in tartaric acid or potassium cyanide gave deposits of copper containing several per cent. of cuprous oxide. Antimony and copper could be simultaneously deposited from a solution of copper sulphate containing tartar emetic, aluminium sulphate, and alkaline tartrate. The alloys were examined, and it is shown that the tendency to form mixed crystals is small, but that rather the two metals separate out as individuals. The electrolysis of a chromium containing copper solution gave no deposit of metallic chromium copper alloy; a copper is deposited which contains about 2.2% of chromium, but this is in all probability present as hydroxide.

J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. IV. Experiments on the Deposition of Iron-Magnesium Alloys from Aqueous Solutions.** ROBERT KREMANN and JOSEF LORBER (*Monatsh.*, 1914, 35, 603—634. Compare preceding abstract).—A series of solutions of ferrous sulphate and magnesium chloride, with and without the addition of potassium chloride, have been electrolysed with the object of in this way obtaining alloys of iron and magnesium. The deposits obtained with current densities varying from 0.6 to 3.3 amperes per sq. dcm. contained metallic iron and a solid solution of iron and magnesium, together with ferrous hydroxide and magnesium hydroxide. The maximum percentage of magnesium in any case being 3.0%, and in all cases where the magnesium approaches this value the oxygen content of the deposit also increases, rising in the stated case to 10.37%. The product oxidises very rapidly in the air, and on slowly drying in a desiccator it becomes heated. On warming the deposit to 200—300° it oxidises so rapidly that it glows. A series of potential measurements were made with the products, and also with electrolytic iron; in all cases the potential against ferrous sulphate solution shows that the iron is passive. The metallographic investigation shows that alongside with the iron deposit there is a silver-white deposit, probably of iron-magnesium alloy and oxides. The determination of the hardness of the deposits leads to the same conclusion. When the dried deposits are placed in water at 94°, an evolution of pure hydrogen occurs, which increases with the magnesium content of the deposit.

J. F. S.

**The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. V. Nickel-Iron Alloys Deposited from Sulphate Solutions at High Temperatures.** ROBERT KREMANN and RUDOLF MAAS (*Monatsh.*, 1914, 35, 731—753. Compare preceding abstracts).—In a previous com-

munication (this vol., ii, 97) iron-nickel alloys deposited at ordinary temperature were shown to be brittle, and this was supposed to be due to the presence of hydrogen. The present paper deals with the production of similar alloys at higher temperatures, the object being to obtain less brittle alloys, which are to be expected if the presence of hydrogen is the cause of the brittleness. Experiments were carried out with (1) solutions of iron and nickel sulphates without additions, (2) in the presence of potassium oxalate, and (3) in the presence of citric acid. In comparison with the results obtained at the ordinary temperature (*loc. cit.*) it is shown that the nickel content of the deposit increases enormously with increasing temperature. With regard to the relationship between the composition of the solution and that of the deposits, it is shown that the same sort of relationships are found as at ordinary temperatures. (1) The nickel content of the deposit increases at first rapidly and then more slowly with an increasing concentration of the nickel in the solution. (2) Addition of potassium oxalate or citric acid increases the nickel content of the deposition. In the case of citric acid the amount of increase depends on the original concentration of the acid. An improvement in the consistency of the deposit by working at higher temperatures is not effected, but the increased percentage of nickel in the deposits (70–80%) is to be regarded as a disadvantage from the point of view of the preparation of nickel steels. When iron cathodes were employed in the electrolysis of the metal there is a great tendency to the formation of spongy deposits, but the use of carbon cathodes leads to a deposit of greater consistency. The concentric ring structure of the alloys found at lower temperatures is obtained in the present work, but much more strongly marked. It is supposed to be due to the formation of hydrogen bubbles on the surface of the deposit round which the further deposition takes place. The hardness of the alloys is greater than that of the alloys obtained at lower temperatures, and from this the authors draw the conclusion that the formation of solid solutions has taken place to a far greater extent at higher temperatures than at lower temperatures. The increased hardness also offers a confirmation to the hypothesis put forward in the earlier paper that the presence of hydrogen cannot be regarded as the cause of the increased hardness of the electrolytic deposits. The *E.M.F.* of the various deposits have been measured against solutions of nickel sulphate and ferrous sulphate. It is shown that both those obtained at 75° and at the ordinary temperature give a potential which is much nobler than the usual potential, and on remaining in the solution slowly approach the normal value. The conclusion is drawn from this that iron-nickel alloys are deposited in the passive condition. This is explained by the assumption of a local alkalinity in the neighbourhood of the electrode.

J. F. S.

**Electrolytic Deposition of Brass on a Rotating Cathode.**  
C. W. BENNETT and A. W. DAVISON (*J. Physical Chem.*, 1914, 18, 488–509).—Since the deposition of brass electrolytically from



mixed solutions of cyanides of zinc and copper only yielded unsatisfactory results, a series of experiments were made with other solutions of salts of these metals with the object of obtaining brass electrolytically. As a preliminary the deposition voltages of zinc and copper, at various current densities, were determined against an oxygen electrode for solutions of the sulphate, formate, fluoride, silicofluoride, and cyanide of these metals with various additions of acid, ammonium chloride, and potassium cyanide, and deposition voltage curves drawn. Pairs of substances which had similar curves were then employed for the production of brass electrolytically. It is shown that in no case save that of the mixed cyanides could a deposit of brass be obtained, and since this is not satisfactory the reasons for the non-success were studied. It is shown that the deposition of brass from cyanide solutions depends probably on two factors: (1) the tendency of the potentials of copper and zinc to become the same in cyanide solutions, and (2) the increase in the potential of the more noble metal by impoverishment. The latter factor is practically eliminated by using a rapidly rotating cathode. A satisfactory brass has not been deposited from cyanide solutions on a rotating cathode; the alloy obtained is brittle, and the brittleness is probably due to occluded impurities which arise from the cyanide, and therefore cannot be removed. The ratio of the metals in the solutions for the deposition of a brass varies with the amount of free cyanide and the rate of rotation of the cathode. J. F. S.

**Magneto-chemical Phenomena.** A. SCHÜCKAREV (*Physikal. Zeitsch.*, 1914, 15, 670—673).—If two platinum plates are immersed in a solution containing 0.1*N*-ferric chloride and 0.1*N*-potassium iodide, a current is obtained when the two plates are connected through a galvanometer. The phenomenon is independent of the stirring of the solution, and if the plates are of unequal size the current flows from the larger to the smaller plate.

If two plates equal in size are employed, and the solution is exposed to the action of a magnetic field in such a way that the two plates are unsymmetrically situated in reference to the magnetic lines of force, a further polarisation current is set up, which flows from the plate which is in the more intense part of the field to the plate in the less intense region. This magneto-chemical effect is not observed if the plates are symmetrically situated with reference to the transverse field or if the plates are at right angles to the lines of force. Similar effects have been obtained with other solutions.

Other experiments are described which show that similar magnetic effects may be observed at the electrodes during the electrolysis of aqueous solutions of certain salts. A table is given in which the results obtained with a larger number of different electrolytes are recorded. H. M. D.

**The Diamagnetic Properties of the Elements follow a Periodic Law.** PAUL PASCAL (*Compt. rend.*, 1914, 158, 1895—1897).—By plotting the coefficients of magnetisation of the elements

against their atomic weights a series of curves are obtained, similar to Lothar Meyer's atomic volume curves, on which elements belonging to the same natural family occupy similar positions on the curves.

W. G.

**Qualitative Method for the Study of the Magnetic Susceptibility of Solutions.** A. QUARTAROLI (*Nuovo Cim.*, 1914, [vi], 7, i, 159—164).—By means of truncated conical poles a field is obtained in which a zone of great intensity is separated sharply from one of feeble intensity. The solution to be examined is introduced into a glass tube of 8—10 mm. diameter, and above it is placed, carefully and without mixing, coloured water. The tube is then arranged between the poles so that the surface of separation of the two liquids corresponds with the lower point where the poles begin to diverge. When the magnet is excited, the water bulges out into the magnetic solution below without sensibly mixing with it, and, if the field is sufficiently intense, a globule of the water becomes detached and remains suspended in the magnetic liquid. The phenomenon is visible with weak fields and dilute solutions, which yield scarcely perceptible indications by Plücker's or the U-tube method. Naturally, the results become more marked as the specific gravities of the two liquids approach equality. T. H. P.

**The Manner in which the Susceptibility of Paramagnetic Substances Depends on the Density.** W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 110—122. Compare this vol., ii. 335).—By application of the quantum theory, the author has deduced equations from which it is possible to calculate the susceptibility of paramagnetic substances. The calculated values for oxygen are in satisfactory agreement with the data obtained by Perrier and Onnes (*loc. cit.*) in their measurements of the susceptibility of liquid mixtures of oxygen and nitrogen. It was previously pointed out that these results could be explained on the basis of Langevin's theory by the assumption of negative molecular fields, and the experiments in question do not therefore afford an *experimentum crucis* in respect of the two theories.

H. M. D.

**Is the Duhem-Margules Equation Dependent on the Ideal Gas Laws?** M. A. ROSANOFF (*J. Amer. Chem. Soc.*, 1914, 36, 1408—1411).—It is shown that the Duhem-Margules equation connecting the partial pressures and the proportions of the components in a binary mixture is a purely thermodynamic relationship, and is applicable to all mixtures independently of whether the vapours satisfy or deviate from the simple gas laws.

H. M. D.

**Laws of Raoult and Henry and the Constants of Ebullioscopy and Cryoscopy.** M. A. ROSANOFF and R. A. DUNPHY (*J. Amer. Chem. Soc.*, 1914, 36, 1411—1418).—The authors show that Raoult's and Henry's laws may be deduced in a simple manner from the Duhem-Margules equation (compare preceding abstract). It is further shown that expressions for the ebullioscopic and cryo-

scopic constants may be obtained from Raoult's law in combination with the gas laws. The molecular rise of the boiling point is given by  $E = RT/100v dP_1/dT$ , in which  $v$  is the specific volume of the vapour at the boiling point and  $dP_1/dT$  is the variation of the vapour pressure with the temperature at the boiling point. From the available data it would seem that both these quantities can be measured with considerable accuracy, and the formula is recommended for the evaluation of boiling-point constants. These constants have been calculated for thirty-three liquids, and it is estimated that the probable error attaching to the values obtained in this way is in general less than 2%.

The expression derived for the freezing-point constant is similar, and may be written  $E = RT/100v(dp_i/dt - dp_w/dt)$ , where  $v$  is the specific volume of the vapour at the freezing point, and  $dp_i/dt$  and  $dp_w/dt$  are the slopes of the vapour-pressure curves for ice and water respectively at this temperature. On account of the experimental difficulty attached to the measurement of these quantities, the equation is only of theoretical interest.

Since Raoult's law follows from the Duhem-Margules equation, in which the molar fractions are based on the molecular weights of the vapours, it is suggested that the molecular weights obtained from boiling-point and freezing-point measurements may have reference to the substances in vapour form, and not to the substances in the liquid solution.

H. M. D.

**Application of the New Heat Theorem to Gases.** W. NERNST (*Zeitsch. Elektrochem.*, 1914, 20, 357-360).—The Nernst heat theorem has hitherto only been applied to condensed systems of crystallised substances, amorphous substances, mixtures, and dilute solutions. The present paper deals with the application to gaseous systems. Three fundamental hypotheses are made: (1) Every gas which is cooled at constant volume without liquefying reaches eventually a condition in which it possesses a vanishing heat capacity. (2) The decrease in the specific heat of a gas occurs earlier the greater the density of the gas; and (3) every physical or chemical change which takes place with the production of the maximum work  $A$  in gases of finite density, occurs in accordance with the expression  $\lim_{T \rightarrow 0} dA/dT = 0$  ( $T = 0$ ). The heat theorem is then applied to the vapour-pressure curve of gases, and the expression  $A = -Tf(\lambda_g/T^2)dT$  evolved. It is shown that every gas which is constantly cooled at constant volume (assuming that liquefaction does not take place) must eventually reach a condition in which it presents resemblances to the amorphous condition. Strong compression of a gas at constant temperature will bring the same condition about. Confirmation of these two statements is found in the results of seismic researches on the conduction of transverse vibrations through the interior of the earth.

J. F. S.

**Specific Volumes of Nickel Steels.** P. CHEVFNARD (*Compt. rend.*, 1914, 159, 53-56).—A study of the dilatation curves of nickel steels with varying nickel content at  $-195^\circ$ ,  $0^\circ$ , and  $750^\circ$ . At  $0^\circ$

there is an irregularity in the curve for alloys between Fe and  $\text{Fe}_2\text{Ni}$ , the alloys corresponding with this portion of the curve undergoing an irreversible transformation, the amplitude of which is proportional to the content of free iron in the alloy. For alloys between  $\text{Fe}_2\text{Ni}$  and  $\text{FeNi}_2$ , there is a reversible irregularity, the amplitude of which is directly proportional to the amount of the compound  $\text{Fe}_2\text{Ni}$  in the alloy.

W. G.

**Calorific Conductivity and Viscosity of Monatomic Liquids.** LÉON BRILLOUIN (*Compt. rend.*, 1914, 159, 27—30).—A mathematical discussion of the subject.

W. G.

**The Limits of Inflammability of Fire-damp.** F. LEFRINCE-RINGUET (*Compt. rend.*, 1914, 158, 1793—1796).—The composition of the combustible gases has been determined, in each case, by Lebreton's apparatus, by Le Chatelier's apparatus, and by the eudiometric method. Using the first apparatus, three factors have to be taken into account, namely, the temperature, the percentage of water vapour, and the solubility of the gases in the water with which they are shaken, the influences of which can be calculated. The results show (1) that pressure exerts no appreciable influence on the limit of inflammability. (2) The limit varies with the diameter of the tube used, and is the limit of propagation relative to the diameter of the orifice. (3) The limit of propagation from the bottom upwards is inferior to the limit from the top of the tube downwards.

W. G.

**The Inflammability of Mixtures of Methane and Different Gases.** F. LEFRINCE-RINGUET (*Compt. rend.*, 1914, 158, 1999—2001).—A study of the inferior and superior limits of inflammability of mixtures of methane and oxygen and nitrogen; and methane, oxygen, and carbon dioxide. The curves obtained, showing in the first  $y = \text{CH}_4/\text{O}_2$  and  $x = \text{N}_2/\text{O}_2$ , and in the second case  $y = \text{CH}_4/\text{O}_2$  and  $x = \text{CO}_2/\text{O}_2$  are the same curves, the abscissæ in the second being multiplied by 0.56. Thus a mixture containing several incombustible gases behaves as though each incombustible element was replaced in a definite ratio by one other of these gases.

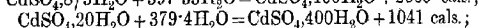
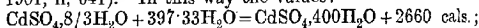
W. G.

**Pressure Regulators. II.** ERNST BRUCKMANN and OTTO LIESCHKE (*Zeitsch. physikal. Chem.*, 1914, 88, 13—21. Compare A., 1912, ii, 534).—Several modifications are described which make the pressure regulator for ebullioscopic determinations more trustworthy and easier to manipulate. Slight changes are made in the method of admitting small quantities of air, and in the automatic regulation of the pressure. Instead of one large flask as compensating volume, two are used in the modified apparatus. A single electrical circuit and relay replaces two such in the original apparatus. By means of this apparatus the pressure can be kept constant to within 6 mm. at pressures down to 100 mm. This constancy of pressure implies a constancy in the boiling point of about  $0.01^\circ$ .

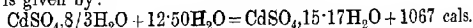
J. F. S.

**Ebullioscopic Behaviour of Solvents at Various Pressures. I. Benzene, Chloroform and Ethyl Alcohol.** FRANZ BECKMANN and OTTO LIESCHE [with JULIUS VON BOSSE] (*Zeitsch. physikal. Chem.*, 1914, 88, 23—34).—The ebullioscopic constants have been determined for the solvents benzene, chloroform, and ethyl alcohol at a series of pressures from 1371 mm. to 40 mm., using a number of substances of known molecular weight in the determinations. The apparatus used was electrically heated, and the pressure was maintained by the manostat previously described (see preceding abstract). The value of the constant falls parallel with the pressure. The constants obtained agree well with those obtained by Drucker (A., 1910, ii, 329), and the values are compared with the values calculated from a number of formulæ which were discussed by the authors (this vol., ii, 170), and in general a satisfactory agreement is found. The newly-determined constants for atmospheric pressure are: benzene, 25·7; chloroform, 38·8; ethyl alcohol, 12·0. Curves are given of the change of the constant with pressure.  
J. F. S.

**The Theoretical Heat of Solution of  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  and the E.M.F. of the Weston Normal Element.** H. VON STEINWEHR (*Zeitsch. physikal. Chem.*, 1914, 88, 229—254).—The work of Holsboer (A., 1901, ii, 226) and that of Kohnstamm and Cohen (A., 1898, ii, 495) on the heat of solution and the solubility minimum of cadmium sulphate are criticised, and the results, in part, recalculated. A series of new determinations of the heat of solution and its temperature-coefficient are made by the method of taking a saturated solution and determining the heat change when successive small quantities of water are added to it. The apparatus and experimental details are the same as that described by the author (A., 1901, ii, 641). In this way the values:



and  $\text{CdSO}_4 \cdot 15 \cdot 17\text{H}_2\text{O} + 5 \cdot 43\text{H}_2\text{O} = \text{CdSO}_4 \cdot 20 \cdot 6\text{H}_2\text{O} + 552 \text{ cal.}$  are obtained, and from these the integral heat of solution of the solid hydrate in 12·5 mols. of water, that is, the number of mols. of water required to give a saturated solution of  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  at 18°, is given by:



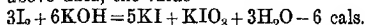
The temperature-coefficient of the heat of solution at 18° is found to be  $-63 \cdot 15$  Cal. From the thermal experiments the total energy of the Weston Element is found to be  $U = 47201$  cals., and from electrical data the E.M.F. is calculated to 1·028675 volt at 18° and  $U$  to 47427 cal. It is thus shown that the energy measured calorimetrically is not independent of the temperature, as was asserted by Cohen (*loc. cit.*), and that the temperature-coefficient is not small enough to be neglected, and the value of this coefficient determined calorimetrically agrees well with that determined electrically.

J. F. S.

The Hypohalogenous Acids and the Hypohalogenites.  
 VII. Heat Changes in Reactions of Iodine Solution. ARON SKRABAL and FRIEDRICH BUCHTA (*Monatsh.*, 1914, 35, 697—730).—Compare A., 1907, ii, 448; 1909, ii, 224; 1911, ii, 382; 1912, ii, 33, 340).—The heat changes accompanying the reactions of iodine in alkali solutions have been determined calorimetrically, using a calorimeter of the Thomsen pattern, in which the usual gold-plated vessels are substituted by glass vessels. The following thermal data has been obtained:

- (1)  $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 3\text{I}_2 + 3\text{H}_2\text{O} + 6\text{KCl} + 829 \text{ cal.}$
- (2)  $\text{KIO}_3 + 8\text{KI} + 6\text{HCl} = 3\text{KI}_3 + 6\text{KCl} + 3\text{H}_2\text{O} + 804 \text{ cal.}$
- (3)  $3\text{KI}_3 + 6\text{KOH} = 8\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} + 25 \text{ cal.}$

From the above data, the value



was deduced, together with the heat of solution of iodine in potassium iodide and in water.

The following reaction, (4)  $\text{KI}_3 + \text{KOH} = 2\text{KI} + \text{HIO} - 43 \text{ cal.}$ , was also determined. In this connexion, note is made of the fact that reactions (3) and (4) occur simultaneously, and the most suitable conditions for each determination were evolved from a knowledge of the kinetics of the reactions. J. F. S.

Principles of the Distillation of Alcohol. E. CHENARD (*Bull. Soc. chim.*, 1914, [iv], 15, 592—595).—The vapour formed by distillation of aqueous alcohol tends to separate into layers of different density, affording a means of mechanical separation. Fractionating columns need not be vertical. It is suggested that partial separation of substances boiling at the same temperature might be effected by taking advantage of the difference in density of the vapour in various parts of the condenser. A. J. W.

The Quantitative Effect of Rapid Cooling on the Constitution of Binary Alloys. II. G. H. GULLIVER (*J. Inst. Metals*, 1914, 11, 252—272).—Methods are given for calculating the proportions of liquid and solid present in rapidly cooled alloys, even in cases in which the liquidus and solidus lines are considerably curved. The methods are illustrated by application to alloys of copper with zinc, tin, and nickel. C. H. D.

Fluidity as a Function of Volume, Temperature, and Pressure. The Equation of State and the Two Kinds of Viscous Resistance. So-called "Slipping" of Gases. EUGENE C. BINGHAM (*J. Amer. Chem. Soc.*, 1914, 36, 1393—1408).—According to Batschinski (A., 1913, ii, 26), the fluidity of a liquid is proportional to the "free volume," and the author shows that this relation also holds for suspensions of solids in liquids. It follows from this connexion between the fluidity and the "free volume" that the variation of the fluidity of a liquid with temperature and pressure may be represented by an equation resembling that of van der Waals. Empirical equations, which may be regarded as

simplified forms of the modified van der Waals equation, have already been shown to represent the experimental data for liquids with considerable accuracy. The equations do not apply, however, to gases, and the large discrepancy between the calculated and observed values is attributed to a special type of viscous resistance which does not come into play in the case of liquids. This resistance has its origin in the diffusion of the gas which carries with it translational motion, and is termed "diffusional viscosity." In liquids, the resistance to flow caused by diffusion is negligibly small in comparison with the "collisional viscosity," which is due to the collisions of molecules of one layer with those of an adjacent layer moving at a slightly lower velocity. In this case, the transfer of momentum is not accompanied by transfer of material.

According to the above views, the viscosity of a gas or liquid is the sum of the diffusional or collisional viscosities. By combining the formulæ for these two types of viscosity, the author arrives at the equation  $\phi = (v - w) / \{A + BT(v - w)\}$  for the connexion between the viscosity  $\phi$ , the specific volume  $v$ , and the absolute temperature  $T$ . In this equation,  $A$ ,  $B$  and  $w$  are constants,  $w$  representing the limiting volume corresponding with zero fluidity (compare Batschinski, *loc. cit.*). It is shown that the fluidity of carbon dioxide in both the liquid and gaseous states can be represented with a fair degree of approximation by means of this formula.

The case of a rarefied gas is also considered in accordance with the above views, and the author draws the conclusion that the viscosity at constant temperature is directly proportional to the density, and at constant volume is directly proportional to the square root of the absolute temperature. At constant temperature and pressure, the viscosity is directly proportional to the square root of the molecular weight, and is independent of the other physical or chemical properties of the gas.

It is supposed that the above deductions from the kinetic theory are also applicable to the explanation of phenomena observed in connexion with the elastic properties of solids. H. M. D.

**Relation of the Internal Pressure of a Liquid to its Dielectric Capacity and Permeability.** W. C. McC. Lewis (*Phil. Mag.*, 1914, [vi], 28, 104-116).—The minimal values of the internal pressure of a number of liquids at 0° have been calculated from the equation  $\pi = RT/(v - v_l)$ , in which  $v_l$  is the limiting volume at absolute zero. This limiting volume has been derived from the critical volume by the relation  $v_l = 0.27v_c$  (Guldberg). In general, the pressures obtained in this way are approximately half as large as the values given by the latent heat of vaporisation.

A comparison of the internal pressures with the corresponding dielectric constants shows that these are not directly proportional, although it is probable that they are related in a less direct manner. On the assumption that the forces of molecular attraction are electromagnetic in character, a relation connecting the internal pressure with the dielectric capacity is deduced, and it is shown

that substances with larger internal pressures have correspondingly smaller permeabilities.

By application of the electron theory to the question of cohesion, it is further shown that the validity of Pascal's relation, according to which the product of the susceptibility and the specific volume is independent of the temperature and the state of aggregation of a substance, involves the conclusion that the orbits of the electrons are constant, and that the frequencies of the absorption bands in the visible and ultra-violet should be the same for both the liquid and gaseous states, which is approximately, but not strictly, in agreement with experiment.

The diminution of cohesion with rise of temperature is in accord with the view that the intermolecular forces are electromagnetic in character.

H. M. D.

**The Variation of the "Gold Value" and the Viscosity of Colloidal Solutions with the Temperature.** L. LICHTWITZ and A. RENNER (*Zeitsch. physiol. Chem.*, 1914, 92, 113—118).—The power of colloidal solutions to prevent the precipitation of gold increases slightly with the temperature. The viscosity diminishes with rise of temperature, and increases again when the temperature falls. The colloidal solutions employed were prepared from gelatin, serum-albumin, and human blood-serum, and the results are in accord with those obtained by previous investigators (compare White, A., 1912, ii, 61).

H. W. B.

**The Viscosity of Protein Solutions. II. Pseudoglobulin and Euglobulin (Horse).** HARRIETTE CHICK (*Biochem. J.*, 1914, 8, 261—280. Compare Chick and Lubrzynska, this vol., ii, 248).—The previous study of the influence of concentration and temperature on the viscosity of solutions of egg and serum albumins has been repeated in the cases of  $\psi$ -globulin and euglobulin, and a general survey of the results is given. In all cases, increase in protein concentration is accompanied by a disproportionately great increase in the viscosity of the solution. The effect is least marked in the case of serum albumin, and is greatest with euglobulin, solutions of which exhibit a high viscosity with a comparatively low protein content. Euglobulin dissolved (dispersed) in alkali has greater viscosity than when dissolved in salt solution. The euglobulin in horse serum is in the condition of salt globulin.

The viscosity of protein solutions is decreased with rise of temperature, frequently to a degree far in excess of that displayed by water or solutions of crystalloids. The greater the viscosity of the solution, the greater is the temperature effect, being most marked in the case of euglobulin solutions.

An interpretation of the results is found in the two-phase nature of the systems studied. The observed disproportionate increase in viscosity of protein solutions with increase in concentration of the protein is explained on the ground that the volume of the disperse phase increases at the expense of the continuous phase.

By means of Hatschek's formula, the amount of water required



for the colloidal solution of 1 gram of these proteins is calculated to be 2.1, 3.8, and 5.8 c.c. for serum albumin,  $\psi$ -globulin, and salt-euglobulin respectively at 25°. Hence, by the withdrawal of water in any salting-out process, the euglobulin, requiring most water, is the first, and serum albumin the last, to be precipitated.

The effect of temperature on the viscosity of protein solutions is explained as being due to a less degree of hydration of the colloid at the higher temperature.

H. W. B.

**Palladium and Hydrogen.** I. ADOLF SIEVERTS (*Zeitsch. physikal. Chem.*, 1914, 88, 103—127).—The absorption of hydrogen by palladium wires of various thicknesses and purity, by palladium sponge, palladium black, and molten palladium has been determined over a range of temperature 100—1500°. It is shown that the absorption by palladium wire decreases with increase of temperature very rapidly up to 600°, and then much more slowly to 800°, and between 800—1500° only very slightly. The quantity of hydrogen absorbed by a given weight of palladium is independent of the area of the palladium surface; consequently, the absorption of hydrogen by palladium is to be regarded as a simple solution. Commercial palladium wire absorbed rather less hydrogen than chemically pure palladium. At the melting point, 1550°, molten palladium absorbed less hydrogen than the solid metal, and consequently there is no formation of bubbles or spitting when molten palladium which is charged with hydrogen solidifies. The absorption of hydrogen by palladium black was investigated with three different specimens between the temperatures 0° and 220°, and the absorption curves were plotted; they were also similar, and showed a very rapid fall in the amount of hydrogen absorbed above 100°. The amount of hydrogen absorbed is different in all the three cases, but the amount absorbed above 137° is larger than that absorbed by palladium wire at the same temperature. On heating, palladium black passes over into palladium sponge, and at the same time there is an increase in the amount of hydrogen absorbed, which at low temperatures approaches that of palladium wire. At temperatures above 600° the absorption of all varieties of palladium is practically identical. An explanation of this is offered in the assumption that platinum black, depending on its method of preparation, is made up of variable quantities of amorphous and crystalline particles. The amorphous variety has a greater power of absorption than the crystalline variety. The change in the absorption by heating is therefore explained as due to the change of the amorphous variety into the crystalline variety. It is supposed that the absorption by the amorphous variety is a simple adsorption, whilst that by the crystalline variety is solution. It is also shown that hydrogen which has been ionised by the action of Röntgen rays or by  $\beta$ - and  $\gamma$ -rays from radium will not diffuse through a palladium plate at the ordinary temperature. J. F. S.

**Adsorption by Hydrated Zirconium Oxide.** E. WEDERKIND and H. RHEINBOLDT (*Ber.*, 1914, 47, 2142—2150).—The hydrated

zirconium oxide was obtained by precipitating a cold, saturated solution of pure zirconium oxychloride with ammonia; the precipitate was collected on a linen filter, washed until the disappearance of the chlorine reaction, and then dialysed to remove the last traces of ammonia. The adsorption of iodine and ammonia by this hydrated zirconium oxide does not follow the ordinary adsorption equation; the absolute content of the adsorbed iodine or ammonia increases with the concentration of the solution, but there is no approximation to a constant value, even in the presence of large excess of the adsorbed substance.

The adsorption of boric acid and phosphoric acid follows the ordinary adsorption law. No salts of zirconium with boric acid are known, but a zirconium hydrogen phosphate exists, namely,  $\text{Zr}(\text{HPO}_4)_2$ ; this phosphate, however, behaves differently from the adsorption compound of hydrated zirconium oxide and phosphoric acid.

Details are given of the qualitative behaviour of hydrated zirconium oxide towards colloidal ferric hydroxide, molybdenum-blue, starch iodide solution, Congo-red, safranin, etc. The solution of Congo-red is rapidly decolorised, with the formation of a blue adsorption compound, which, on warming, is transformed into the red salt.

T. S. P.

**Adsorption of Dextrose. II.** PETER RONA and KOLOMAN VON TÓTH (*Biochem. Zeitsch.*, 1914, 64, 288—295. Compare A., 1909, ii, 381).—It has been shown that the disappearance of sugar from solutions when the latter are shaken with animal charcoal, for the purpose of clearing, can be avoided by the addition of acetic acid and other substances to the solution. Experiments show that in the case of acetic acid this is due to the undissociated molecules, and is not a function of the hydrion concentration. Experiments with the urethane series of substances show, furthermore, that the more readily a substance is adsorbed, the more readily it sets free sugar from its state of adsorption with the charcoal. The action of various substances in the sugar-charcoal mixture is due, therefore, to their mechanical adsorbability.

S. B. S.

**Sorption of Certain Acids and Non-electrolytes by Wool.** A. DIETL (*Kolloid. Zeitsch.*, 1914, 14, 319—321).—The absorption of various substances from aqueous solution by wool has been investigated by experiments at different concentrations. The relation between the quantity of substance  $c_f$  removed by a fixed weight of wool, and the equilibrium concentration  $c_w$  of the aqueous solution, is expressed by the equation  $\sqrt{c_w}/c_f = \text{constant}$ . For phosphoric acid  $n=2$ , benzoic acid  $n=1.77$ , salicylic acid  $n=2.15$ , acetone  $n=1.47$ , sucrose  $n=1.1$ . The low values of  $n$  for the two non-electrolytes are supposed to indicate the formation of a solid solution.

H. M. D.

**The Dissociation Pressures of Some Nitrides.** R. E. SLADE and G. I. HIGSON (*Rep. Brit. Assoc.*, 1913, 451).—The following

nitrides dissociate, at the given temperatures, at pressures which are not greater than the given values: vanadium,  $1203^{\circ}$ , 0.2 mm.;  $1271^{\circ}$ , 1.5 mm.; tantalum,  $1170^{\circ}$ , 0.4 mm.; boron,  $1222^{\circ}$ , 9.4 mm.  
C. H. D.

**Dissociation Pressures of Ammonium and Tetramethylammonium Haloids and of Phosphonium Iodide and Phosphorus Pentachloride.** ALEXANDER SMITH and ROBERT PAYTON CALVERT (*J. Amer. Chem. Soc.*, 1914, 36, 1363—1382).—The dissociation pressures were measured at a series of temperatures by means of the static isothermometer. In the case of phosphorus pentachloride, the dynamic isothermometer was employed, on account of the difficulty of finding a suitable confining liquid. The limiting temperatures and pressures are indicated in the following summary, which also shows (in brackets) the temperatures at which the dissociation pressure is equal to 760 mm.: ammonium bromide, 300— $403^{\circ}$ , 35—935 mm. ( $394.6^{\circ}$ ); ammonium iodide, 310— $410^{\circ}$ , 48—857 mm. ( $404.9^{\circ}$ ); ammonium chloride, 250— $350^{\circ}$ , 50—1063 mm. ( $337.8^{\circ}$ ); tetramethylammonium chloride, 190— $233.3^{\circ}$ , 120—760 mm. ( $233.3^{\circ}$ ); tetramethylammonium iodide, 240— $307^{\circ}$ , 81—799 mm. ( $305.5^{\circ}$ ); phosphonium iodide, 19.2— $65.7^{\circ}$ , 50—900 mm. ( $62.6^{\circ}$ ); phosphorus pentachloride, 90— $167^{\circ}$ , 18—919 mm. ( $162.8^{\circ}$ ). The experimental data can be satisfactorily represented by the Kirchhoff-Rankin-Dupré formula,  $\log p = -A/T + B \log T + C$ , in which  $A$ ,  $B$ , and  $C$  are constants. The values of the constants for each of the substances are recorded in the paper.  
H. M. D.

**The Ludwig-Soret Phenomenon.** AUGUST EILERT (*Zeitsch. anorg. Chem.*, 1914, 88, 1—37).—A glass apparatus is described, of 20 sq. cm. horizontal cross-section, for containing the liquid. The upper part is heated by a flat glass spiral near the surface, containing mercury and conveying a current. The lower part is cooled by a similar spiral of silver tube, through which cold water circulates. It is possible to keep the upper layer at a temperature constant within  $0.5^{\circ}$  for twelve hours. The solutions are separated after the experiment by cautiously opening a tap in the lower part of the apparatus.

The apparatus ensures the presence of a narrow zone quite free from convection currents. About eighteen hours are required for the system to reach the stationary state. The ratio of concentrations in the upper and lower zones,  $c_o/c_u$ , is then determined by analysis. Equilibrium may also be reached from the other side by using two solutions, the initial ratio of concentrations being greater than the ratio to be expected. Diffusion then takes place from the colder to the hotter region. These two methods are employed in each experiment, the equilibrium thus being reached from both sides.

For solutions of sodium, potassium, and strontium chlorides, acetic acid, and sucrose in water, and of benzil in benzene and lithium chloride in acetone, the ratio  $c_o/c_u$  is greater the greater the concentration, whilst for solutions of lithium chloride in water

and of acetic acid in nitrobenzene it is nearly independent of the concentration, and for hydrochloric acid it increases with diminishing concentration. In the case of the chlorides examined, the ratio increases with the molecular weight of the solute. Increasing the difference of temperature between the two layers increases the ratio of concentrations for solutions of acetic acid or sucrose in water, diminishes it for solutions of acetic acid in nitrobenzene, and is almost without influence for solutions of lithium chloride in water.

The explanation of the Ludwig-Soret phenomenon given by van't Hoff (A., 1888, 778) is thus incorrect. The results may be qualitatively explained, but only for concentrated solutions, by Tammann's hypothesis of the internal pressure.

C. H. D.

**Counter Diffusion in Aqueous Solution.** WILLIAM ALEXANDER OSBORNE and LILIAS CHARLOTTE JACKSON (*Biochem. J.*, 1914, 8, 246—249).—The authors have found that if there are two solutions, one vertically placed above the other in a tall cylinder and in contact over a relatively small surface, and if both contain  $N/10$ -sodium chloride, and the lower of them contains in addition ammonium sulphate, dextrose, or some other substance, then, after some days' diffusion, the concentration of sodium chloride in the upper fluid is greater than it is in the lower. No satisfactory explanation of these results is offered.

H. W. B.

**The Relation between Ionic Mobility and Ionic Volume.** RICHARD LORENZ (*Kolloid. Zeitsch.*, 1914, 14, 322).—A claim for priority against Mines (compare this vol., ii, 418) in respect of the view that the abnormally high mobility of the hydrogen and hydroxyl ions may be due to interaction between the ions and the solvent water molecules (compare A., 1913, ii, 281).

H. M. D.

**Processes Operative in Solutions. XXIX. Disturbance of the Equilibrium in Solutions by "Strong" and "Weak" Interfering Agents.** H. E. ARMSTRONG and E. E. WALKER (*Proc. Roy. Soc.*, 1914, A, 90, 375—393. Compare A., 1913, ii, 368).—Further experiments have been made in which the change in the rotatory power of levulose on the addition of foreign substances has been investigated. On the assumption that the change in rotation is due to an alteration in the proportion of the  $\alpha$ - and  $\beta$ -forms, the results obtained indicate that monohydric alcohols and most weak solutes (hormones) favour the formation of  $\alpha$ -levulose, whilst polyhydric alcohols, sugars, salts, phenols, and basic substances (anhormones) are favourable to the formation of  $\beta$ -levulose.

In connexion with the effects which are produced by interfering agents, an attempt is made to distinguish between (1) a purely mechanical screening effect, which causes dissociation of the water complexes, of the complex molecules of the solute, and of the hydrates of the solute, and (2) an action of opposite character, which is proportional to the attractive powers or residual affinities of the admixed substances, and promotes association. It is claimed that the hypothesis is justified by the explanation which it affords of interference effects in general.

H. M. D.

**Rhythmic Crystallisation. Liesegang's Rings and Related Phenomena.** III. ERNST KÜSTER (*Kolloid. Zeitsch.*, 1914, 14, 307—319. Compare A., 1913, ii, 893).—A detailed description is given of the microscopic structures which are obtained when a small quantity of an aqueous solution is allowed to evaporate in contact with a layer of solidified gelatin solution. The structure varies markedly with the nature of the dissolved substance, as may be seen by comparison of the microphotographs obtained with solutions of trisodium phosphate, copper sulphate, ferrous sulphate, ammonium sulphate, and potassium ferrocyanide. On the one hand, the microphotographs afford evidence of simple ring-formation, similar to that exhibited by the precipitation layers in the interaction of silver nitrate with a solidified layer of gelatin containing small quantities of potassium chromate, whilst others exhibit a net-like or grating structure. In the author's opinion, the cause of the formation of the structures is the same, although specific influences come into play in the different cases. Although the development of the micro-structure is facilitated in presence of a gelatin or other gel, it is improbable that the gel plays a fundamental rôle in the phenomenon. H. M. D.

**Ring Formation and Crystal Structure.** P. GROTH (*Ber.*, 1914, 47, 2063—2067).—Although the results of recent experiments with Röntgen rays have clearly proved that molecules do not exist in crystals, yet it is evident from the frequent occurrence of close morphotropic relationships between chemically related substances, especially in the case of benzenoid compounds, that some of the interatomic linkings of the molecule must persist in the crystal. In view of the special rôle apparently played by the ring system of benzene, an inquiry has been started to ascertain whether aliphatic ring compounds, such as anhydrides and imides of dibasic acids, will behave similarly.

It is found that there is a close structural resemblance between crystals of the anhydrides of succinic and maleic acids, whereas the acids themselves show no such relationship. There is also a close similarity revealed, when their topic parameters are calculated, between the imides of succinic and *cis-s*-dimethylsuccinic acids.

E. H. R.

**Manipulation of the Immersion Ultramicroscope.** R. ZSIGMONDY and W. BACHMANN (*Kolloid. Zeitsch.*, 1914, 14, 281—295).—A new form of ultramicroscope is described in which the immersion objectives of both the illuminating and observing systems are of large aperture. In comparison with the slit ultramicroscope, the new instrument affords a much greater intensity of illumination and facilitates appreciably the investigation of the ultramicroscopic particles of hydrosols. The method of setting up the apparatus and the manipulation involved in ultramicroscopic observations are described in detail. H. M. D.

**A Modification of the Ultra-filtration Apparatus.** P. KIRSCHBAUM (*Biochem. Zeitsch.*, 1914, 64, 495—498).—The apparatus

which is illustrated by figures, is essentially a modification of Elfer's, and consists of a metal bell-jar screwed on to a metal under-part supported on a tripod which bears the sieve support for the filter. This is made of silver, as is also a hollow cylinder which is placed in the upper bell-jar and fixes on to the sieve. Into this the liquid to be filtered is brought, and it is the most essential modification of the apparatus.

S. B. S.

[The Preparation of Colloidal Solutions by Electric Disintegration]. RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1914, 88, 22). Compare Zavriev, this vol., ii, 444).—It is shown that Bredig (A., 1900, ii, 278) had previously prepared colloidal solutions of cadmium and zinc by electric disintegration. His method, however, differs essentially from that of Zavriev (*loc. cit.*) in many particulars.

J. F. S.

Behaviour of Gels towards Liquids and the Vapours Thereof. II. L. K. WOLFF and E. H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 92—101. Compare A., 1913, ii, 568).—According to von Schroeder (A., 1903, ii, 721), a gelatin plate which has taken up the maximum quantity of water in contact with the liquid, loses water when introduced into a space saturated with water vapour at the same temperature. Although the authors' earlier experiments (*loc. cit.*) seemed to confirm this observation, further experiments by an improved method, in which the swollen gelatin plate was exposed to the influence of a current of air saturated with water vapour at the temperature of swelling, show that the weight of the gelatin plate remains unchanged. Under the conditions of the previous statical method of experimentation, it has been shown that pure liquid water loses weight by evaporation, and although the static method has been modified so as to eliminate to a large extent the errors which are incidental to this method, it is much inferior to the dynamic method of observation. The results obtained with gelatin have been confirmed by experiments with agar-agar and with celloidin swollen in ethyl alcohol.

It would seem that the vapour pressure of gelatin which has taken up a relatively small amount of water is practically equal to that of pure water. In consequence of the very small difference in vapour pressure, the absorption of water from the saturated vapour is extremely slow, and a condition of equilibrium is apparently reached when this is not really the case. There is consequently no discrepancy between the phenomena associated with the swelling of gelatin and the second law of thermodynamics, as was previously supposed.

H. M. D.

Silver Chromate Rings and Spirals. RAPHAEL ED. LIESENG (*Zeitsch. physikal. Chem.*, 1914, 88, 1—12).—The author shows that the production of a rhythmic precipitation of silver chromate in gelatin jellies is best effected when silver nitrate is allowed to diffuse into potassium chromate jellies which contain definite

small quantities of acid and gelatose. The commoner commercial varieties of gelatin contain these substances in practically the necessary concentration, but gelatin which has been washed with water must have the necessary quantity of acid, either citric acid or nitric acid, added to it, and hard gelatin must be mixed with gelatose for the purpose of showing the formation of rings. The presence of a large hydrogen-ion concentration in rich chromate jellies causes the rings to be formed at greater distances from one another, the reason for this being the increased solubility of the silver chromate. Small disturbances cause the precipitation to occur in spirals instead of concentric rings, and often portions of a spiral are formed in isolated positions, which later join up with the main system. The Ostwald supersaturation theory (*Zeitsch. physikal. Chem.*, 1897, **23**, 365) can be applied to the formation of spirals in the same way as in the case of the formation of rings.

J. F. S.

**Structure of Silicic Acid Gels.** JOHN S. ANDERSON (*Zeitsch. physikal. Chem.*, 1914, **88**, 191—228).—A quantity of silicic acid gel was prepared and dried until the weight was constant by keeping over concentrated sulphuric acid. It was found that it contained 5.5% of water, which was not removable at the ordinary temperature. The dried gel was then placed in contact with the vapour from sulphuric acid-water mixtures in an exhausted apparatus, and in each case the increase in weight noted. The reverse process was then carried out; the gel, saturated with water, was placed in contact with sulphuric acid of increasing concentration up to pure sulphuric acid, and in each case the weight determined. In this way a series of values of the amount of water absorbed or given up at different vapour pressures was obtained. Curves were plotted, and it is shown that the absorption and drying curves do not coincide over their whole length, there being a decided hysteresis shown in the sense that water is given up at lower pressures than those at which it is absorbed. In this way measurements were obtained over the pressure range for the water vapour of 12.7—0 mm. Similar experiments were made with alcohol and benzene. In the case of alcohol, mixtures of alcohol and glycerol were employed to obtain alcohol vapour pressures from 32.6—0.0 mm., and in the case of benzene, mixtures of benzene and paraffin oil gave benzene vapour pressures from 60—0 mm. Curves of exactly the same type were obtained as in the case of water. The water experiments were repeated by the van Bemmelen method (*A.*, 1908, ii, 838; 1909, ii, 234), which consisted in hydrating and dehydrating the gels in a desiccator in the presence of air. Curves of almost the same type were obtained, except that by this method the curve in the region where hysteresis is shown is horizontal. This is not the case in the absence of air, and points to the fact that the gel is made up of pores of varying sizes, which are largest at the point where hysteresis begins and smallest where it ceases on the dehydrating curve. From measurements of the lowering of the vapour pressure of water, alcohol,

and benzene in the gel, the values of the diameter of the pores are calculated to the following figures: (a) largest diameter,  $5.49\ \mu\mu$ ,  $5.17\ \mu\mu$ , and  $5.98\ \mu\mu$ ; (b) smallest diameters,  $2.75\ \mu\mu$ ,  $2.42\ \mu\mu$ , and  $2.70\ \mu\mu$  in the three cases respectively. The dimensions of these values are in agreement with those obtained by Zsigmondy from other properties of the gel (A., 1911, ii, 880). The specific gravities of the gel substance ( $\text{SiO}_2$ ), the dried gel, and the gel saturated with water have also been obtained, and found to be 2.048, 0.980, and 1.500 respectively. The velocity at which the three substances water, alcohol, and benzene are absorbed and given up by the gel were determined and compared. Very similar curves are obtained for all three cases. It is shown that the absorption and expulsion of liquids from gels, as well as the turbid appearance at certain stages, are to be explained by capillary phenomena, and that there is no evidence of hydrate formation.

J. F. S.

**Swelling of Vulcanised Caoutchouc.** F. KIRCHHOF (*Kolloidchem. Beih.*, 1914, 6, 1—22. Compare Posnjak, A., 1912, ii, 912).—The swelling of plantation Para-caoutchouc has been examined by measuring the increase in weight of thin disks of the material after immersion in benzene, carbon tetrachloride, carbon disulphide, and benzene (D 0.74) for measured intervals of time.

The results show that the maximum swelling of the caoutchouc decreases as the extent of the vulcanisation increases. The maximum swelling was attained after twenty-four hours. The specific influence of the various liquids runs parallel with the solvent capacity for caoutchouc. The rate at which swelling takes place is approximately in agreement with the equation for a unimolecular change. The swelling velocity increases with rise of temperature, but the temperature-coefficient is very small (1.1). The relation between the extensibility and the vulcanisation-coefficient is similar to that existing between the swelling capacity and the degree of vulcanisation. Although the swelling is in part due to capillary absorption, the observed increase in weight is mainly due to solution of the solvent in the caoutchouc.

Some experiments were also made on the swelling of the caoutchouc disks in the vapours of the boiling liquids. This effect is very much smaller, and is practically independent of the degree of vulcanisation.

H. M. D.

**Dynamic Isomerism.** H. E. ARMSTRONG, T. M. LOWRY, SYDNEY YOUNG, C. H. DESCH, J. J. DOBBIE, and M. O. FORSTER (*Rep. Brit. Assoc.*, 1913, 141—143).—A report on work published during 1913.

C. H. D.

[The Condition Diagram of Water.] G. TAMMANN (*Zeitsch. physikal. Chem.*, 1914, 86, 57—62. Compare Bridgman, this vol., ii, 254).—Polemical; an answer to Bridgman's criticism (*loc. cit.*) of the author's paper (A., 1913, ii, 935), in which the existence of



two forms of ice II is described. The author has repeated his experiments, with results which confirm the original work.

J. F. S.

**Equilibria in Ternary Systems.** XV. F. A. H. SCHREINKMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 70—85. Compare this vol., ii, 548).—A further examination of types of equilibrium in ternary systems, the assumption being made that the vapour contains only one or two of the three components.

H. M. D.

**Equilibrium Distribution of Certain Neutral Narcotics.** ALFRED DORNER (*Chem. Zentr.*, 1914, i, 1453—1454; from *Sitzungsber. Heidelberger Akad. Wiss.*, 1914, [B], 1—12).—According to Warburg, it may be assumed that the concentrations of different narcotics of differing "external concentration" are the same or similar at the affected point in the cell when a similar action is produced. The author's investigations on the equilibrium distribution of acetone, heptyl alcohol, and octyl alcohol, using intact "vogelerythrocytes" and their stomata, lead to the following conclusions: The stomata, after being freed from fat, are able to fix considerable quantities of narcotics, the amount being greater for the more powerful narcotics than for the weaker ones. The stomata which have not been treated with alcohol and ether fix considerably more octyl alcohol than the extracted substance. The difference may either be attributed to the fixative power of the fatty constituents of the stomata as compared with that of the nucleohistone, or to a possible alteration of the latter by treatment with alcohol and ether in such a manner that it can fix less of the alcohol. The fixation of narcotics by the stomata is not a chemical process, and the equilibria measured are more closely allied to adsorption than to distribution equilibria. 'H. W.'

**Conditions of Formation and Existence in Equilibrium with Solutions of Basic, Acid and Complex Salts.** E. I. SCHEPITALSKI (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 566—576).—The author applies the considerations previously discussed (A., 1907, i, 695) to the investigation of complex equilibria in solutions, with special reference to chromates.

From the facts known concerning the dependency of the composition of a precipitated salt on the degree of acidity of the solution, the conclusion is drawn that, for each salt, there exist two definite concentrations of acid between which the given salt may exist in the solid state in equilibrium with the solution. The conversion of a basic salt into a normal one, or the latter into an acid one, may be regarded as a reversible reaction of combination with a molecule of acid,  $M_1 + A \rightleftharpoons M_2$ . From this it follows that, for saturation of the solution simultaneously with the two salts,  $M_1$  and  $M_2$ , there should exist the relation  $S = M_2/M_1 = \text{constant}$ . The constancy of  $S$  is related to the non-dissociated molecules of acid, and  $S$  will correspond with the hydrolytic tension of the mutual

transformation of the salts, the simultaneous existence of which is possible only for the particular magnitude of  $S$ . For any solution saturated with respect to two hydrolysable salts, capable of inter-conversion, the concentration of the non-dissociated acid depends only on the temperature. It is shown, further, that the possibility of formation of each salt is defined by two quite definite magnitudes, termed "stability products," characteristic of the particular salt.

T. H. P.

**Equilibria of Reduction of Oxides by Carbon.** R. E. SLADE and G. I. HIGSON (*Rep. Brit. Assoc.*, 1913, 450—451).—The equilibrium pressures have been determined when certain oxides are heated with carbon, the free metal being present in excess. With three components, M, C, and O, there are four phases, CO, M, MO, and either C or  $M_2C$  (M being two equivalents of the metal). Equilibrium is reached from both sides. The following values are obtained:

Vanadium .....	1340°	1.5 mm.
Tantalum .....	1270	< 0.1 "
Chromium .....	1292	6.2 "
" .....	1339	9.2 "
Tin .....	750	> 760 "
Tin, in presence of silica .....	753	670 "

C. H. D.

**Equilibrium in the System Arsenic Tribromide and Naphthalene.** N. A. PUSCHIN and J. F. KRIGER (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 559—565).—Thermal analysis of the system arsenic tribromide-naphthalene shows that these components form a definite yellow compound,  $C_{10}H_8 \cdot 2AsBr_3$ , m. p.  $19.8^\circ$ . There are two eutectic points: (1) one at  $17.2^\circ$  occurring in the stable region and corresponding with 19.5 mol. %  $C_{10}H_8$ ; (2) the other in the unstable region at  $10^\circ$ , corresponding with 27 mol. %  $C_{10}H_8$ . A transition point occurs at  $19.8^\circ$ , the corresponding composition being 33 mol. %  $C_{10}H_8$ . On reciprocal dissolution the two components retain their normal molecular weights.

T. H. P.

**Freezing-point Curves of Volatile Systems.** GEORGES BAUME (*J. Chim. Phys.*, 1914, 12, 206—215. Compare A., 1912, ii, 329, 1039).—General observations in reference to the author's investigation of the freezing-point curves of a large number of volatile binary systems.

H. M. D.

**Quantitative Investigation of Volatile Systems. Freezing-point Curve of the System Sulphur Dioxide-Water.** GEORGES BAUME and (Mlle.) ALINE TYKOCINER (*J. Chim. Phys.*, 1914, 12, 270—275).—Sulphur dioxide and water are only partly miscible at low temperatures. The region covered by the two-liquid system extends from about 11 to 97 mols. % of sulphur dioxide. The data obtained for systems containing less than 11 mols. % of sulphur dioxide agree with those recorded by Roozeboom (*Rec. trav. chim.*,

1884, 3, 44; A., 1886, 117). The eutectic at which ice and the compound  $\text{SO}_2 \cdot 7\text{H}_2\text{O}$  co-exist in equilibrium lies at about  $-3^\circ$ . The freezing-point curve of this compound is intercepted at  $+12.1^\circ$  by the straight line which corresponds with one of the above-mentioned liquid phases. The freezing temperature of the second liquid is  $-74^\circ$ , and the corresponding straight line on the diagram intercepts the curve for sulphur dioxide (m. p.  $-72.3^\circ$ ) at about 97 mols. % of sulphur dioxide.

Some observations relating to the systems  $\text{HCl} + \text{H}_2\text{O}$ ,  $\text{NH}_3 + \text{H}_2\text{O}$  are also included in the paper. H. M. D.

**Quantitative Investigation of Volatile Systems.** Freezing-point Curves for the Systems formed by Hydrogen Chloride and Methyl Alcohol with Methyl Chloride and by Methyl Alcohol with Water. GEORGES BAUME and WACŁAW BOROWSKI (*J. Chim. Phys.*, 1914, 12, 276—281).—The freezing-point data for mixtures of methyl alcohol and water correspond with the intersection of two curves at  $-139^\circ$  and about 67 mols. % of methyl alcohol. Mixtures which contain from 55 to 75 mols. % of methyl alcohol yield non-crystalline glasses on cooling. The previous results obtained by Pickering for mixtures containing 0—50 mols. % of alcohol are in agreement with the authors' data.

Hydrogen chloride and methyl chloride also afford the simplest possible thermal diagram. The eutectic lies at  $-161^\circ$  and 27.3 mols. % of methyl chloride.

Methyl alcohol and methyl chloride behave in exactly the same way, the eutectic temperature being  $-112^\circ$ , and the composition corresponding with 24.2 mols. % of methyl chloride. H. M. D.

**The System  $\text{CaSiO}_3\text{--MnSiO}_3$ .** ST. KALLENBERG (*Centr. Min.*, 1914, 388—394).—The freezing-point curve for mixtures of calcium and manganese silicate is continuous, and shows a minimum at  $1150^\circ$  for a mixture containing 10 mols. % of calcium silicate. Within the limits of experimental error the results are in agreement with those obtained by Ginsberg (A., 1908, ii, 842). Since artificial wollastonite is either hexagonal or monoclinic, whilst rhodonite is triclinic, it is probable that the mixed crystals form an isodimorphous series.

Although the crystalline form of synthetic rhodonite is very similar to that of the naturally occurring rhodonites, it differs from the minerals in the positive character of its double refraction. Synthetic rhodonites containing iron and magnesium silicate are optically similar to the pure manganese silicate, but in presence of 5% of calcium silicate the positive double refraction changes to negative. Since the natural rhodonites generally contain calcium silicate in greater proportion than this, the apparent discrepancy in the optical behaviour of synthetic rhodonite and the minerals is readily explained. H. M. D.

**Mixed Crystals in the Ternary Systems Formed by Strontium Chloride, Barium Chloride, and Sodium Chloride or Potassium Chloride.** ERHARD VORTISCH (*Jahrb. Min. Bek. B.*, 1914, 38, 185—272).—The equilibrium relations in the binary and

ternary systems have been determined by freezing-point measurements combined with the investigation of the microscopic structure of the products of crystallisation.

Strontium chloride and barium chloride form a complete series of regular ( $\beta$ ) mixed crystals, which on cooling are transformed into monoclinic ( $\alpha$ ) crystals. These two series correspond with the  $\alpha$ - and  $\beta$ -forms of barium chloride, which co-exist in equilibrium at  $922^\circ$ . The freezing-point curve shows a minimum at  $847^\circ$ , at which point 30 mols. % of barium chloride are present.

Sodium chloride and strontium chloride are immiscible, and the two freezing-point curves meet at  $565^\circ$  and the composition 50 mols. % of strontium chloride. Sodium chloride and barium chloride behave similarly, the eutectic in this case being at  $654^\circ$  and 40 mols. % of barium chloride.

The corresponding ternary system is characterised on the space model by means of which the experimental data are summarised, by the existence of three surfaces of saturation, the solid phases corresponding with which are sodium chloride,  $\alpha$ -mixed crystals, and  $\beta$ -mixed crystals of strontium and barium chloride respectively.

Potassium chloride combines with strontium chloride to form the compounds  $2\text{KCl}, \text{SrCl}_2$ , melting at  $597^\circ$ , and  $\text{KCl}, 2\text{SrCl}_2$ , melting at  $638^\circ$ . With barium chloride it forms the compound  $2\text{KCl}, \text{BaCl}_2$ , melting at  $660^\circ$ . The compounds  $2\text{KCl}, \text{SrCl}_2$  and  $2\text{KCl}, \text{BaCl}_2$  are isomorphous, and rhombic crystals containing both compounds separate out from certain fused ternary mixtures. Mixed crystals of the type  $\text{KCl}, 2(\text{SrBa})\text{Cl}_2$  are also formed.

By reason of the fact that this system gives rise to four series of mixed crystals, the equilibrium relations are much more complicated than those exhibited by the ternary system, in which the potassium chloride is replaced by sodium chloride. The spacial model showing the equilibrium relations is characterised by five surfaces which determine the conditions under which crystallisation of  $\alpha(\text{SrBa})\text{Cl}_2$ ,  $\beta(\text{SrBa})\text{Cl}_2$ ,  $\text{KCl}, 2(\text{SrBa})\text{Cl}_2$ ,  $2\text{KCl}, (\text{SrBa})\text{Cl}_2$ , and  $\text{KCl}$  occur. For a detailed account of the relationships between the various systems the original must be consulted. H. M. D.

**Natural Fats from the Point of View of the Phase Rule. III. The Ternary System: Tristearin-Stearic Acid-Palmitic Acid.** ROBERT KREMANN and RICHARD KROPSCH (*Monatsh.*, 1914, 35, 561–580. Compare A., 1912, ii, 1152; 1913, ii, 922).—Of the three binary systems making up the above-mentioned ternary system, one, that between tristearin-palmitic acid, has been investigated by de Visser (A., 1898, i, 560) and Carlinfanti and Levi-Malvano (A., 1910, i, 5). The fusion curves for the remaining binary systems are determined in the present work. The system tristearin-stearic acid is simple, and possesses a single eutectic point at  $54^\circ$  for the mixture 90% tristearin, 10% stearic acid. The system tristearin-palmitic acid gives a fusion curve which rises rapidly from tristearin and passes through a flat maximum at 7% palmitic acid, and at 16% palmitic acid has a eutectic point at  $63^\circ$  (not sharp); then passes along a very flat maximum to a second eutectic

point at 50% palmitic acid at 55°, and then rises linearly to the melting point of palmitic acid. A series of other fusion curves are then determined for ternary mixtures, taking a series of constant ratios of two constituents, and varying the third; in this way some fourteen series are determined, tables and curves are given for each of these, and the separate curves are combined in a triaxial diagram to give the ternary system. From these results it follows that of the hard fats, i.e., those which are free from oleic acid and triolein, those which correspond with the system tristearin-palmitic acid, and particularly those with a small palmitic acid content, will have the highest melting points. J. F. S.

**Velocity of Absorption of Hydrogen and Oxygen by Solutions of Metallic Salts.** JOHN EGGEAT (*Zeitsch. Elektrochem.*, 1914, 20, 370—381).—The velocity of absorption of hydrogen and oxygen by reducible and oxidisable salt solutions respectively has been determined at 17°. It is shown that the reduction and oxidation of ter- and bi-valent iron by hydrogen and oxygen took place with its maximum velocity when the platinum which served as stirrer and catalyst was brought into contact with the gaseous atmosphere above the solution. It is shown that the maximum velocity is proportional to the surface of the platinum and the time during which it is in contact with the gas space, but is independent of the number of times per minute it is raised into the gas space and lowered into the liquid. The initial velocity of absorption, under uniform conditions, is constant and independent of the nature of the dissolved metal salt; as the reaction approaches completion a decrease in velocity of absorption occurs, which is generally exponential. The meaning of this phenomenon is explained on the basis of a separation of the process into a velocity of occlusion and a velocity of "activation" of the occluded gas towards the solution. The beginning of the process appears to be governed by occlusion, that is, by the nature of the platinum, whilst at the end of the process the different powers of "activation" of the various metals make themselves noticeable. The velocity of occlusion has a temperature-coefficient of 1.8—3.3%, and is independent of the concentration. A decrease in the absorption is to be noticed, which runs parallel with the increased viscosity of the solution. The effects are also not independent of the nature of the anions and the hydron concentration. Solutions of  $\text{Fe}^{\text{III}}$ ,  $\text{U}^{\text{VI}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{Ti}^{\text{IV}}$ ,  $\text{Mo}^{\text{VI}}$ , and *p*-benzoquinone are reversibly reduced by hydrogen and reoxidised by oxygen. The velocity of autoxidation of solutions in alkali, to which quantities of tartrate have been added, increases in the order  $\text{V}^{\text{III}}$ ,  $\text{Mo}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Sn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ , and  $\text{Mn}^{\text{II}}$ . J. F. S.

**Kinetics of Chemical Reactions. IX.** E. I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 535—559).—In the oxidation of hypophosphorous acid by means of iodine, the value of the velocity-constant, calculated on the assumption that the reaction is one of the first order, continually increase with the time; the initial value of the constant is, however, approximately proportional

directly to the concentration of the sodium hypophosphite, and inversely to that of the iodine. The results have therefore been calculated according to the equation  $dx/dt = k(A-x)(B+x)$ . If the concentration of hypophosphite remains constant, increase of the concentration of iodine is accompanied by increase of  $B$  and decrease of  $k$ , but is not proportional to  $B$ . A similar result has been obtained in other instances where the above equation is applicable.

When the quantity of iodine used is larger than is required for oxidation of the hypophosphorous to phosphoric acid, the early observations are in agreement with a reaction of the first order, whereas later the value of the constant begins to fall, and the formula  $dx/dt = k(A - mk)$  becomes applicable. These results are discussed in relation to the equation

$$dx/dt = k_1(A-x) + k_2x(A-x) - k_3x(A-x),$$

previously deduced by the author (A., 1913, ii, 681).

The results obtained cannot be explained according to the formula  $O:PH_2-OH$ , for hypophosphorous acid, which initially unites with the iodine. It is therefore assumed that in acid solution the above form exists in equilibrium with  $OH:PH-OH$ , the latter not being found in alkaline solution, in which oxidation by iodine does not take place. The course of the reaction is explained on the assumption that the complex  $HI_3$  or  $I_2, HI$  under-

goes partial dissociation in an aqueous medium into



and  $H^+$ .

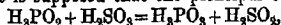
Unlike hypophosphorous acid, phosphorous acid is only slowly oxidised by iodine, and the reaction does not proceed to an end. The numerical results show that the oxidation takes place according to the equation  $dx/dt = k(A - kx) - k_1x$  or

$$dx/dt = k(A - mx).$$

The magnitude of  $k_1$  depends on the concentrations of the phosphorous acid and of the iodine, but that of  $k$  is approximately constant. Here, too, the author assumes the existence of molecules of the two structures  $O:PH(OH)_2$  and  $P(OH)_3$ , only the latter undergoing oxidation by means of iodine into phosphoric acid.

Investigation of the reduction of sulphurous acid to sulphur by hypophosphorous acid shows that the separation of sulphur occurs only after the lapse of some time, and that if an aqueous solution of safranin or indigotindisulphonic acid is added to a solution of hypophosphorous and sulphurous acids containing sulphuric acid, the liquid becomes decolorised appreciably earlier than the sulphur is deposited. The conclusion is therefore drawn that this reduction of sulphurous acid takes place by way of intermediate products, such as hyposulphurous acid, to which is due the decolorisation of the safranin or indigotindisulphonic acid. The formation of sulphur requires the accumulation of a certain quantity of hypsulphurous acid, which in an acid medium undergoes change according to the equation  $2H_2SO_3 = H_2SO + H_2SO_3$ , this being followed rapidly by  $H_2SO = H_2O + S$ . Calculation of the velocities of the

reduction by means of the formula  $Ak = x/t(A - x)$  shows that, after the lapse of a certain time, and subsequent to the initial precipitation of sulphur, the magnitude of  $Ak$  remains constant. The amount of sulphurous acid which disappears during the early stage of the reaction is greater than that calculated for a reaction of the second order. It is supposed that the principal change,



is at first accompanied by the formation of a product of combination of the two acids,  $O:PH_2 \cdot OH + HSO_2 \cdot OH = OH \cdot SO_2 \cdot PH_2(OH)_2$ , this compound existing in solution for some time, and then decomposing into its original constituents. Of the three reactions,  $H_3PO_2 + H_2SO_3 = H_3PO_3 + H_2SO_2$ ,  $2H_2SO_2 = H_2SO + H_2SO_3$ , and  $H_2SO = H_2O + S$ , it is the first which determines the second order of the reaction, the other two occurring very rapidly.

The reduction of safranine in a solution of sulphurous and hypophosphorous acids takes place according to the equation

$$dx/dt = k(A - x)(B + x),$$

and that of indigotindisulphonic acid according to

$$dx/dt = k(A + x)(B + x).$$

T. H. P.

**The Velocity of Solution of Zinc-Blende and Galena in Dilute Sulphuric Acid.** FELIX ROSENKRÄNZER (*Zeitsch. anorg. Chem.*, 1914, 87, 319—334).—The crushed ores (galena from Claustal, and four varieties of blende) are sifted and graded, and treated with dilute sulphuric acid by shaking in a flask, after which the dissolved hydrogen sulphide is estimated colorimetrically by the method based on the formation of methylene-blue (this vol., ii, 380).

The experiments show that the velocity of solution is constant throughout an experiment, and is proportional to the concentration of the sulphuric acid and to the surface of the particles. The concentrations employed are 1.25, 0.125, and 0.0125%. The influence of temperature is independent of the size of the particles, and is represented by an exponential function. The temperature-coefficient is the same for blende and galena, although the velocities are very different. The difference of velocities, and the fact that rapid shaking is without influence on the velocity, are opposed to the view that the velocity of a heterogeneous reaction is merely a diffusion velocity. A chemical process must precede the actual solution.

C. H. D.

**Kinetics of the Thermal Bleaching of Colouring Matters.** S. VAVILOV (*Zeitsch. physikal. Chem.*, 1914, 88, 35—45).—The velocity at which the dyes cyanine, lepidine-cyanine, quinaldine-cyanine, and pinaverdol are bleached by the action of heat has been investigated at temperatures from 60° to 110°, and the results are compared with the photochemical bleaching of the same substances obtained by Lasarev (*A.*, 1912, ii, 219, 513). The dyes were mixed with collodion and poured on thin squares of glass, and subjected to the action of heat in a specially constructed thermostat. They were investigated from time to time by means of a König-Mertens

spectrophotometer. The bleaching of lepidine-cyanine takes place in accordance with the equation for a bimolecular reaction, and that of cyanine with the unimolecular equation. The order of the reaction in the other cases could not be determined. The temperature-coefficient of all the reactions approximates to 3, whereas that for the photochemical reaction is only slightly larger than unity. The solid, coloured products of the thermal bleaching show little difference optically from that of the products of the photochemical bleaching, and the difference can be explained by changes in the colloidion. The gaseous products of the reaction and atmospheric air are shown to influence a strong catalytic action on the process. Experiments on the thermal bleaching of the dyes in the absence of colloidion led to no positive results. J. F. S.

**Catalysed Ester Formation in Mixed Solvents by means of Hydrogen Chloride.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1914, 88, 63—102).—The velocity of esterification of benzoic acid, succinic acid, tartaric acid, and malic acid has been determined in alcoholic hydrogen chloride, and in mixtures of alcohol-benzene, alcohol-ether, and alcohol-carbon tetrachloride. Experiments were made also in the same mixtures to which known amounts of water had been added. The equivalent conductivity of the hydrogen chloride in all the solutions used for the kinetic experiments was also determined. It is shown that the velocity of esterification in absolute alcohol is reduced by the addition of the other solvents, most in the case of ether and least in the case of carbon tetrachloride. The retarding influence of water is approximately the same in the alcohol-ether mixture as in the case of absolute alcohol, and greater in the alcohol-carbon tetrachloride mixture. The constants calculated to a constant quantity of alcohol, in the cases of mixtures of aqueous alcohol and the ether-absolute alcohol mixture, are smaller than those for mixtures to which a second solvent has not been added, but in the cases of mixtures of alcohol and carbon tetrachloride and those containing more than 25% benzene they are larger, and increase with an increasing amount of the second solvent. The influence of the addition of benzene to alcohol in the esterification of succinic, malic, and tartaric acids is similar to that observed in the case of benzoic acid, and the irregularities lie in the opposite direction to that which they should lie if the esterification in these cases is termolecular, that is, does not take place in steps. Just as in absolute alcohol, so in the various mixtures, the esterification proceeds as a reaction of the first order. It is also shown that the equivalent conductivity of hydrogen chloride in absolute alcohol and in aqueous alcohol is reduced by the addition of the other three solvents. If it is assumed that the catalytic action of the hydrogen ion is greater than that of the undissociated hydrogen chloride, then it follows that the addition of these other solvents to the alcohol has an accelerating influence on the esterification. If, however, it is assumed with Sneathlage (A., 1912, ii, 947; 1913, ii, 1044) that the undissociated hydrogen chloride molecule is twice as active as the hydrogen ion, then it



follows that the addition of benzene and carbon tetrachloride alone acts in an accelerating manner, and that only when they are present in large quantity and when only traces of water are present. If it is assumed that the concentration of the unimolecular alcohol is determinative of the velocity of esterification, then this would explain the accelerating influence of the other solvents, although the specific action of these solvents and that of the acid itself would also play some part in the acceleration.

J. F. S.

**Catalytic Influence of Copper Oxide on the Combination of Oxygen and Hydrogen.** JACQUES JOANNIS (*Compt. rend.*, 1914, 159, 64—67. Compare this vol., ii, 260).—Pure iron wire at 300° does not act as a catalyst on an explosive mixture of oxygen and hydrogen. It becomes coated with a film of black oxide, which is not reduced under the given conditions. Electrolytic copper at 300° or even at 200° is at first oxidised in the explosive mixture, and the oxide formed acts as a catalyst for the combination of the oxygen and hydrogen. Copper oxide itself undergoes no reduction, but at 300° produces practically complete combination of the hydrogen and oxygen. The catalytic action is, however, apparently largely controlled by the vapour tension of the water formed.

W. G.

**Catalytic Actions of Colloidal Metals of the Platinum Group. X. The Reduction of the Oxides of Heavy Metals.** C. PAAL [with WILHELM HARTMANN and GUSTAV BRÜNNES] (*Ber.*, 1914, 47, 2202—2216).—When a colloidal solution of cupric hydroxide is reduced by means of colloidal palladium, prepared according to Paal's method, and hydrogen, a colloidal solution of copper is obtained. A similar solution results when precipitated copper hydroxide is used instead of the colloidal solution, in this case reduction and peptonisation occurring at the same time. The colloidal copper solution is ruby-red in transmitted light, and black in reflected light (compare Paal and Leuze, A., 1906, ii, 356). In one case where only a small quantity of colloidal palladium was used, colloidal cuprous oxide was obtained as an intermediate product. In order to increase the stability of the solutions, it is best to add some sodium protalbate to the reaction mixture, to act as a protective colloid. In a similar manner colloidal nickel can be obtained from a colloidal solution of nickel hydroxide, or from the precipitated hydroxide, but with the latter the reduction is not complete. The metal hydrosol is a brilliant, chestnut-brown colour in transmitted light, and black in reflected light; the reversible gel forms blackish-brown, brittle lamellæ.

Cobaltous and lead hydroxides could not be reduced similarly to those of copper and nickel.

Experiments on the reduction of solutions of ammonium chromate, metavanadate, and molybdate gave respectively the colloidal solutions of chromic hydroxide, vanadium trihydroxide, and molybdenum tetrahydroxide. The first is a blackish-green, the second a brown, and the last a reddish-brown hydrosol; all give

reversible gels. Ammonium tungstate is not reduced by colloidal palladium and hydrogen.  
T. S. P.

The Quantum Theory and the Rotation-energy of Molecules. EVA VON BAHR (*Phil. Mag.*, 1914, [vi], 28, 71—83).—The author discusses the application of the quantum theory to phenomena associated with the rotational energy of molecules, and shows that considerable support for the assumption of discontinuity in the distribution of the rotation-frequencies is afforded by the results which have been obtained in experiments on the ultra-red absorption of gases (compare A., 1913, ii, 810). These results are summarised with special reference to their significance for the quantum theory.  
H. M. D.

Atomic Structure and the Spectrum of Helium. J. W. NICHOLSON (*Phil. Mag.*, 1914, [vi], 28, 90—103. Compare this vol., ii, 325).—The theory of atomic structure put forward by Bohr (A., 1913, ii, 689, 943, 1045) must, in the author's opinion, stand or fall according to its capacity to give an account of the spectra of hydrogen and helium. It is shown that the theory cannot explain the helium spectrum or any other series spectrum by any modification which retains the simpler theory of hydrogen and the Pickering series, if it is assumed that forces act between bound electrons. The assumption that such forces do not exist is also shown to lead to conclusions which are incompatible with the helium spectrum. From these results the author infers that Bohr's theory cannot be developed in the manner which its earlier success in the interpretation of spectra appeared to foreshadow. It is to be admitted, however, that the connexion between the Rydberg constant and Planck's constant is so close that it is difficult to believe that this connexion is not real. Such reality does not, however, involve a corresponding reality in the process by which the form of the hydrogen spectrum is derived on the basis of Bohr's theory.  
H. M. D.

Presidential Address to Section B (Chemistry). W. P. WYNN (*Rep. Brit. Assoc.*, 1913, 408—424).—A review of the following subjects: residual valency; substitution in the paraffin series; the structure of the benzene molecule; substitution in the benzene series; symmetric and asymmetric syntheses.  
C. H. D.

Quantity of Residual Valencies Possessed by Various Molecules. A. P. MATTHEWS (*J. Physical Chem.*, 1914, 18, 474—487).—A theoretical paper in which the amount of residual valency of a number of non-associated liquids and gases has been calculated by subtracting the number of valencies known to be acting in the molecule from the calculated total number of valencies. The difference between the two values is regarded as the residual valency. The total number of valencies is calculated from the molecular cohesion by means of the formula  $a = C(M \times N)^{2/3}$ , in which  $a$  is the van der Waals factor,  $C$  a constant which is calculated to

$3.2015 \times 10^{-37}$  expressed in dynes from Millikan's new determination of the number of molecules in a gram-molecule,  $M$  the molecular weight, and  $N$  the total number of valencies. The value of  $a$  was obtained from the formula  $a = \{(S^3 - S + 2)/(S - 2)\} P_c V_c^2$ , in which  $S$  is the critical coefficient,  $P_c$  and  $V_c$  the critical pressure and volume respectively (compare A., 1913, ii, 674). The constant  $C$  for a pair of molecules was assumed to be equal to  $(m^2 k)^{2/3}$ , in which  $m$  is the gravitational mass of a molecule of unit molecular weight, and  $k$  the gravitational constant. The assumption is made that at a given moment only a small percentage of the molecules are exhibiting residual valencies, so that the figures calculated really give mean values. The numbers obtained vary between 0.195 for hydrogen and 9.08 for *n*-octane.

J. F. S.

**The Solidification of Metals from the Liquid State.** C. H. DESCH (*J. Inst. Metals*, 1914, 11, 57-118).—A report and summary under the following heads: the cellular structure of metals; crystallisation from centres and the formation of crystallites; foam-structures and Quincke's hypothesis; cellular structures in cooling liquids; liquid crystals; the influence of surface tension; undercooling and the existence of a metastable limit; changes of volume on solidification; the thrust exerted by growing crystals.

C. H. D.

**The Influence of Time in the Rapid Deformations of Metals.** GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1914, 158, 1969-1973).—By varying the height of fall of the weight producing deformation in metal bars by shock, from 6 metres to 1 metre, a variation in the time of deformation from 0.001 to 0.01 of a second has been obtained. This variation produces practically no difference on the work absorbed by rupture of the bar as measured by its resilience. Grooved bars were used, and care was taken in their preparation to ensure that the results obtained in the experiments came between two well-defined limits, which did not differ much from one another.

W. G.

**Simple Extraction Apparatus.** MICHAEL FREUND (*Chem. Zeit.*, 1914, 38, 802).—The apparatus consists of a small, wide-mouthed bottle closed with a cork, through which pass a tube connected with a reflux apparatus and a siphon tube; the former tube is provided with a side-tube, and this and the outer end of the siphon are bent downwards, and pass through a cork closing a flask containing the solvent. The material to be extracted is placed in the bottle, and the condensed solvent from the reflux apparatus falls through the material; when the bottle is full of solvent the siphon comes into operation, and the solution is returned to the solvent flask.

W. F. S.

**Simple Fat Extractor.** G. A. STOKES (*Analyst*, 1914, 39, 295).—The substance to be extracted is placed in a paper thimble, covered with a layer of cotton-wool, and the thimble is then inserted

in the flask containing the solvent by means of a wire, the lower part of which is bent into the form of a spiral so as to fit tightly into the thimble. The upper part of the wire passes through the cork closing the flask, and the latter is attached directly to a reflux apparatus. At the commencement of the extraction the lower part of the thimble is immersed in the boiling solvent, but after a time it is raised by means of the wire and the extraction continued.

W. P. S.

**Apparatus for the Extraction of Powdery Material.** ERNST BORNEMANN (*Chem. Zeit.*, 1914, 38, 833. Compare A., 1913, ii, 855).—A central tube made from porous material is placed down the centre of the thimble holding the substance to be extracted and contained in a Soxhlet apparatus; the lower end of the tube passes through the bottom of the thimble, and extends into the stem of the apparatus; the latter is not provided with a siphon. The top of the tube is plugged with cotton-wool, and the condensed solvent from the reflux apparatus is distributed over the thimble by means of a perforated glass bulb and ring fitted above the central tube.

W. P. S.

**Modification of Golodetz's Rectifying Apparatus for Mixtures of Low Boiling Point.** W. NEUBERGER (*Chem. Zeit.*, 1914, 38, 823. Compare A., 1912, ii, 626).—A reflux apparatus is provided above the side-tube of the jacket surrounding the still-head of the apparatus; the condensed liquid passes back through the still-head into the flask, while the less volatile vapours escape into the condenser.

W. P. S.

**Non-uniformity of Drying Oven Temperatures.** LORIN H. BAILEY (*J. Ind. Eng. Chem.*, 1914, 6, 585).—Thermometric readings of the temperatures at different parts of various drying ovens (electrically-, gas-, and steam-heated ovens) showed that only those surrounded by boiling water and steam are capable of maintaining even approximately uniform temperatures.

W. P. S.

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## Inorganic Chemistry.

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**The Taste of Hard Water.** ALEXANDER FRIEDMANN (*Chem. Zentr.*, 1914, i, 1515—1516; from *Zeitsch. Hyg. Infekt. Krankh.*, 77, 135—142).—In connexion with the supposed superiority in taste of a hard water when compared with a soft water, the author has carried out experiments with carbon dioxide dissolved in distilled water. Less than 116 mg. of carbon dioxide per litre can never be tasted; between 116 and 246 mg. give different effects with differ-

ent persons, whilst more than this quantity is distinctly tasted. The temperature of the solutions varied between  $15^{\circ}$  and  $17^{\circ}$ . In the case of hard water, bicarbonate-carbon dioxide and total carbon dioxide were examined by Winkler's method. Carbon dioxide in hard water can be tasted at lower concentrations than in distilled water. In one case, the presence of 52.5 mg. of carbon dioxide per litre in a water of  $36.4^{\circ}$  hardness at  $14.2^{\circ}$  was recognised, whilst a water containing 173 mg. of free carbon dioxide per litre was found to be distinctly acidic. Above this concentration, carbon dioxide is practically invariably detected by taste. In distilled water, on the other hand, suspicion is first aroused by 126 mg., and the uncertainty persisted in one case up to 252 mg.; more than 264 mg. per litre is detected by taste with certainty. Below this concentration, the free acid is not tasted as such, but can nevertheless cause the sensation termed "refreshing." The possible reason of this property is discussed.

H. W.

**Physical Analysis of Some Springs at Evaux-les-Bains.** CLUZET and TH. NOGIER (*Compt. rend.*, 1914, 159, 92—93).—The authors have determined for some five of the springs at Evaux-les-Bains the following physical constants: (a) Temperature at the source; (b) density; (c) freezing point, (d) electrical resistance; (e) radioactivity measured in millimicrocuries of radium emanation from one litre of water at the source. The gases evolved from the Caesar spring have a high radioactivity, and there is a large evolution of gas in one year (262,000 litres).

W. G.

**Composition of the Water of the "Limans" of Odessa.** ET. BARAL (*Bull. Soc. chim.*, 1914, [iv], 15, 630—634).—Complete analyses of the water of three salt lakes on the shore of the Black Sea are given. The number of grams per litre of residue at  $120^{\circ}$  from each lake is as follows: Konialnick, 82.684; Kadjibeiski, 45.410; Klein-Liebenthal, 21.674.

A. J. W.

**Influence of the Current Frequency and Temperature on the Yield of Ozone.** N. PUSCHIN and M. KAUCHTSCHEV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 576—590).—With constant periodicity, up to 800 per second, the yield of ozone increases with increase of the voltage from 6500 to 8000. When the frequency is varied, but the voltage and other conditions kept constant, the yield of ozone increases as the frequency is increased to 1240 periods per second at 6500 volts, to 950 at 7000 volts, and to 660 at 8000 volts; if the rate at which the air passes through the ozoniser remains the same, increase of the frequency beyond these limits is accompanied by diminution of the yield of ozone. Continued increase of the air current displaces the maximum yield towards continually increasing frequencies. Rise of temperature from  $0^{\circ}$  to  $28^{\circ}$  causes the yield of ozone to increase, but further rise diminishes it.

T. H. P.

**Theory of the Lead Chamber Process.** WALTHER HEMPEL (*Zeitsch. angew. Chem.*, 1914, 27, 407—408).—A reply to Wentzki (this vol., ii, 558), in which it is pointed out that the objection that no account had been taken of the thermal dissociation of nitrogen peroxide, and that the gas had been led into the reaction chamber at the ordinary temperature in the experiments on the velocity of the formation of sulphuric acid (A., 1914, ii, 455), is quite groundless. The entry and exit tubes of the reaction chamber were wound with electrically heated wires, and thereby maintained at a temperature slightly higher than that of the chamber itself, and condensation of the sulphuric acid in the tubes was likewise prevented by this arrangement.

G. F. M.

**Two New Modifications of Phosphorus.** P. W. BRIDGMAN (*J. Amer. Chem. Soc.*, 1914, 36, 1344—1363).—During the course of experiments on the effect of high pressure on white phosphorus it was found that this is transformed into a new modification. The transition temperature is a linear function of the pressure, and varies from  $-76.9^{\circ}$  at a pressure of 1 kilogram/cm.<sup>2</sup> to  $64.4^{\circ}$  at a pressure of 12,000 kilogram/cm.<sup>2</sup>. The results obtained in the dilatometric measurements were confirmed at atmospheric pressure by thermometric observations. By crystallisation of solutions of white phosphorus in carbon disulphide at low temperature, the new modification was obtained in the form of microscopic crystals belonging to the hexagonal system.

In an attempt to convert white phosphorus into red by the application of high pressure, a black modification of phosphorus was obtained. The conversion, which is irreversible, takes place quite readily at  $200^{\circ}$  under a pressure of 12,000 kilogram/cm.<sup>2</sup>. Black phosphorus is characterised by its high density. By the suspension method this was found to be 2.691 at the ordinary temperature, whilst the density of white phosphorus is 1.83, and that of red phosphorus varies from 2.05 to 2.34 according to the method of preparation. It is not spontaneously inflammable, and may be heated to about  $400^{\circ}$  in the air without igniting. When heated in a closed tube, it vaporises and condenses in the colder parts to red and white phosphorus. In this behaviour it closely resembles red phosphorus, and it would seem that the vapours of black and red phosphorus are identical. In its general chemical behaviour it is also very similar to red phosphorus. In contrast with the white and red modifications, black phosphorus is a fairly good conductor of heat and electricity. The resistivity at  $0^{\circ}$  was found to be 0.711, and this diminishes as the temperature rises. On account of the porous character of the substance, the true value of the specific resistance is probably considerably less than this number would indicate. Between  $30^{\circ}$  and  $100^{\circ}$  the specific heat was found to be 0.170, which is appreciably less than the recorded values for red phosphorus over the same interval of temperature. The relationship between the specific heats would seem to show that black phosphorus is more stable than red. This conclusion is supported

by the vapour-pressure data, according to which the black modification is much less volatile than the red.

By heating white phosphorus to a dull red heat under a pressure of about 1000 kilogram/cm.<sup>2</sup> it is transformed into red phosphorus, the density of which (2.387) is greater than that of "metallic" phosphorus (2.34), which represents the densest form of red phosphorus previously obtained.

The connexion between the different modifications is discussed, with special reference to the nature of red phosphorus, and the relation between this and the black and white forms. H. M. D.

**Preparation of Phosphorus Pentachloride.** SAMUEL PRAOCEK (Fr. Patent, 463497).—When calcium phosphate and sodium or potassium chloride, in the proportions  $\text{Ca}_3\text{P}_2\text{O}_8 + 10\text{KCl}$ , are heated together in a closed vessel at, say, 1100°, and the small amounts of phosphorus trichloride and chlorine formed are removed by an aspirator so that their partial pressures in the vessel remain below atmospheric pressure, a rapid and almost complete reaction occurs, giving  $3\text{CaO} + 5\text{K}_2\text{O} + 2\text{PCl}_5$ . The phosphorus pentachloride may be collected, but is preferably passed into hot water, and so converted into phosphoric and hydrochloric acids, the latter being then separated by evaporation. From the residue potassium hydroxide is obtainable. T. H. P.

**The Melting Point of Arsenic.** W. HEIKE (*Intern. Zeitsch. Metallographie*, 1914, 6, 168—171).—By using a sealed porcelain vessel, as for the lead-arsenic alloys (this vol., ii, 464), and enclosing this in an outer vessel packed into sand, it has been found possible to determine the melting and freezing points of arsenic. The value found is 830° (compare Goubau, this vol., ii, 198; Jolibois, *ibid.*). Arsenic which has solidified in the porcelain vessel tarnishes readily in air, whilst the crystals condensed from vapour are very stable. C. H. D.

**Borates. II and III. The System  $\text{BaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  at 30°.** U. SBOGRI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 717—721, 854—857. Compare this vol., ii, 562).—The author's experiments were carried out by determining analytically the equilibria reached at 30° by mixtures of various borates with water and boric acid or barium hydroxide. The borates taken had the compositions  $\text{BaO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$ ,  $2\text{BaO}, 3\text{B}_2\text{O}_3, 6\text{H}_2\text{O}$ , and  $\text{BaO}, 3\text{B}_2\text{O}_3, 7\text{H}_2\text{O}$ . The resulting solubility curves are represented on a triangular diagram. R. V. S.

**The Identification of Silicic Acids.** G. TSCHERMAK (*Zeitsch. anorg. Chem.*, 1914, 87, 300—318).—A reply to criticisms. Mügge (A., 1908, ii, 277, 688) gave experiments to show that the position of the break in the dehydration curve varied with the temperature. Some of these results show the break in the curve quite clearly at the point predicted by theory, when the velocity of dehydration is plotted, whilst others are useless for calculation, owing to the intervals of time being too large, and to other errors.

In many cases the mineral or synthetic product used as source of silicic acid is not homogeneous, so that mixtures of silicic acids are obtained. It is necessary to avoid preliminary treatments, such as pressing or prolonged washing, which alter the structure of the gel. The dehydration should be carried out over sulphuric acid of known concentration. Theile's experiments (this vol., ii, 138), when these fail to yield true results for the constitution of the silicates examined, are vitiated by errors of the kind described above. Control experiments, and an optical examination of Theile's preparations, show that some of the silicates were not homogeneous. The homogeneous products yield silicic acids, corresponding closely with the requirements of Tschermak's theory. The replacement of water in silicic acid gels by other liquids, although proving that the gels are adsorption compounds, does not disprove the original presence of definite hydrates.

C. H. D.

**Colloidal and Gelatinous Carbon.** N. L. SÖHNGEN (*Chem. Weekblad*, 1914, 11, 593—596).—Electrolysis of a solution of potassium hydroxide with a current of 4 amperes at 100 volts, using carbon electrodes, yields a substance containing about 81·2% C, 0·85% H, and 18% O. The product obtained by the action of sulphuric acid on a solution of sucrose contains about 55% C, 4·5% H, and 41% O. Colloidal carbon cannot be prepared by either method, or by any known process.

A. J. W.

**A Reduction of Carbon Monoxide by Hydrogen brought about by Radium Emanation.** OTTO SCHREUER (*Compt. rend.*, 1914, 158, 1887—1889).—A mixture of carbon monoxide and hydrogen submitted to the influence of radium emanation for nineteen days undergoes a diminution in volume of nearly 10%. The gas left at the end has no odour, and is shown to be a mixture of carbon monoxide and hydrogen with a small amount of methane and probably a trace of ethylene. The gas contains neither formaldehyde nor methyl alcohol. During the first few days a slight solid deposit was noticed on the walls of the experimental flask, but this had disappeared at the end of four days. On repeating the experiment, formaldehyde was detected in the flask at the end of two days. The action, therefore, probably takes place in two stages, the carbon monoxide being first reduced to formaldehyde, which is then in its turn reduced to methane and other hydrocarbons.

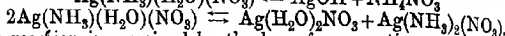
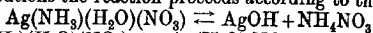
W. G.

**Preparation of Ammonium Sulphate.** BADISCHE ANILIN- & SODA-FABRIK (Fr. Patent, 463487).—The slow oxidation of ammonium sulphite to sulphate is considerably accelerated by keeping the solution alkaline with ammonia and by the presence of oxygen-carriers. The reaction proceeds well under pressure. T. H. P.

**Does a Mono-ammoniacal Silver Nitrate Exist?** A. REYNOLDS (*Bull. Soc. chim. Belg.*, 1914, 28, 198—200. Compare A., 1904, ii, 403).—The amount of silver hydroxide precipitated from solu-



tions of silver nitrate containing various quantities of ammonia is determined for a number of solutions. The author considers that in dilute solutions the reaction proceeds according to the equations:



The reaction is examined by the law of mass action, and from the results it is shown that it is extremely probable that a mono-ammoniacal silver nitrate does exist.

J. F. S.

**The Dehydration of Gypsum.** C. GAUDEFROY (*Compt. rend.*, 1914, 158, 2006—2008).—Anhydrous calcium sulphate as prepared by the dehydration of gypsum is much more soluble and less dense than the natural anhydrite. The last stage in the dehydration, passage from the hemihydrate to the anhydrous form, is reversible, each process only requiring a few minutes at 110° in a dry and humid atmosphere respectively. The temperature at which the anhydrous sulphate is produced therefore depends on the hygrometric state of the air in the oven, thus explaining the variations in the results of different workers. Further, both the hemihydrate and the anhydrous form can absorb water vapour from the air at the ordinary temperature. The author considers that the two types of figures formed on gypsum by its dehydration are only modifications of one another, and are formed by the hemihydrate.

W. G.

**Glucinum Borates.** B. BLEYER and L. PACZUSKI (*Kolloid. Zeitsch.*, 1914, 14, 295—306).—Experiments have been made to ascertain whether any glucinum borates are formed as the products of reactions in which water is involved, for theory indicates that borates can only be obtained in this way if the borates themselves are not very soluble and the corresponding oxides or hydroxides are readily soluble.

In the first series of experiments, the distribution of boric acid between water and glucinum hydroxide was investigated. On account of the rapidity with which the hydroxide ages and diminishes in its reactivity, it was found necessary to make the experiments with glucinum hydroxide precipitated *in situ* by the addition of ammonia to a solution containing boric acid and glucinum sulphate. The results obtained in this manner show that the ratio of distribution of the boric acid between the water and glucinum hydroxide is independent of the concentration of the boric acid. This constancy of the concentration ratio was found both in experiments at 20° and at 100°. From this behaviour, the authors draw the conclusion that no definite compounds are formed by the interaction of glucinum hydroxide with aqueous solutions of boric acid, and that the boric acid removed by the hydroxide forms a solid solution.

A further series of experiments, in which the products obtained by the interaction of glucinum sulphate and sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) in aqueous solution were investigated, confirms this con-

clusion. The composition of the solid solution, which separates out when these solutions are brought together, varies considerably with the concentration and with the relative proportions of the reacting substances. Precipitates containing the largest proportion of boric acid are obtained when the glucinum salt reacts with an equivalent quantity of sodium borate in a solution of the highest possible concentration. The addition of sodium or ammonium sulphate to the solution has no appreciable influence on the composition of the precipitate.

According to the results of this investigation, it is extremely probable that the glucinum borate,  $5\text{BeO} \cdot \text{B}_2\text{O}_3$ , described by Krüss and Mohrat (A., 1890, 697), is simply a solid solution of boric acid in glucinum hydroxide.

H. M. D.

**Magnesium Chloride. II. Influence of Magnesium Chloride on the Oxidising Action of Chlorates and Nitrates.** K. A. HOFMANN, FRITZ QUOOS and OTTO SCHNEIDER (*Ber.*, 1914, 47, 1991—1999).—In continuation of former experiments (Hofmann and Höschele, this vol., ii, 204), the authors have found that moist magnesium chloride considerably facilitates a number of technically important oxidation processes. When chlorates, nitrates, and nitrites are mixed with magnesium chloride, either in the form of the hydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , or as carnallite mother liquors, their oxidising action takes place at remarkably low temperatures, the molten magnesium chloride keeping the mixture homogeneous, and the water preventing too great a rise in temperature. As an example, the oxidation of anthracene to anthraquinone may be cited. A mixture of 20 grams of anthracene, 23 grams of sodium nitrate, and 80 grams of magnesium chloride hexahydrate is heated in an open flask on the sand-bath. The fusion turns yellow already at  $125^\circ$ , owing to the formation of anthraquinone. The temperature is allowed to rise to  $145^\circ$ , 40 c.c. of water added, and the temperature slowly raised to  $300^\circ$ , stirring well meanwhile. The anthraquinone separates above the salt residues, and after being collected is mixed with 5 grams of magnesium oxide and sublimed. The yield is 91.5%.

Details are also given of the influence of moist magnesium chloride on the oxidation of aniline to aniline-black, of a mixture of aniline and paraphenylenediamine hydrochloride to indulines and paraphenylene-blue, of a mixture of *p*-tolylenediamine hydrochloride, aniline, and *o*-toluidine to safranin, and of the oxidation of sawdust and of molasses to oxalic acid. Considerable quantities of trimethylamine are first evolved in the oxidation of the molasses. Magnesium chloride also has a considerable influence on the introduction of nitroso-groups into phenols, and on the formation of induline from a mixture of aniline, aniline hydrochloride, and aminoazobenzene; the previous preparation of aminoazobenzene is not absolutely necessary; it also accelerates the liberation of iodine from potassium iodide solutions by means of potassium chlorate and dilute sulphuric acid.

Magnesium chlorate and nitrate also exert an oxidising action at

comparatively low temperatures in the presence of water of crystallisation, but the temperatures are not so low as with the mixture of magnesium chloride hexahydrate and sodium nitrate.

The experiments of the authors lead them to the conclusion that the effect of the hydrated magnesium chloride cannot be ascribed to its products of hydrolysis or to the ions formed. It is possible that additive products are formed, which are very reactive. Magnesium salts are known to give complex compounds very readily.

T. S. P.

**The Crystallographical and Optical Properties of Magnesium and Manganese Pyrophosphates.** O. ANDERSON (*J. Washington Acad. Sci.*, 1914, 4, 318—325).—The two salts are found to belong to a new monosymmetric isomorphous group. Crystals for examination were obtained from cavities in a rapidly crystallised fusion of each substance. The optical properties could only be determined on microscopic fragments.

$\text{Mg}_2\text{P}_2\text{O}_7$ :  $a:b:c = 0.7947:1:1.0880$ ;  $\beta = 75^\circ 49'$ ; optical character positive;  $D_D^{20} 3.058$ .

$\text{Mn}_2\text{P}_2\text{O}_7$ :  $a:b:c = 0.7834:1:1$ ;  $\beta = 74^\circ 9'$ ; optical character positive;  $D_D^{20} 3.707$ .

The two salts are perfectly miscible in the solid state, forming a system belonging to Roozeboom's Type I.

E. H. R.

**Allotropy of Zinc.** II. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 59—60. Compare this vol., ii, 127).—The so-called "atomised" zinc obtained by Schoop's method has been found by dilatometric observations to consist of a mixture of two or more allotropic forms. The metal was found to contract at  $25^\circ$ .

H. M. D.

**Allotropy of Cadmium.** II. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 54—58).—In a previous paper (this vol., ii, 52) experiments were described which seemed to show the existence of a transition temperature at  $64^\circ$ . Further dilatometric observations indicate, however, that this temperature varies with the previous thermal history of the metal, and the authors draw the conclusion that there are more than two allotropic forms which must be taken into account.

H. M. D.

**Allotropy of Cadmium.** III. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 122—131. Compare preceding abstract).—According to dilatometric observations, electrolytically deposited cadmium is unstable at the ordinary temperature, and its nature has been further investigated by electromotive force measurements. The *E.M.F.* of the cell, electrolytic cadmium | cadmium sulphate solution | 1% cadmium amalgam, was found to be 0.0503 V at  $25^\circ$ , but after standing for several weeks the *E.M.F.* fell to  $0.0475^\circ$ . The change in the *E.M.F.* is attributed to the transformation of unstable  $\gamma$ -cadmium into the stable  $\alpha$ -form. In support of this view, it was

found that the above difference in *E.M.F.* increases from 2.8 millivolt at 25° to 4.0 millivolt when the temperature is lowered to 0°. This is to be expected, for the difference in *E.M.F.* should increase as the interval between the temperature of the measurement and the transition temperature is increased.

In addition to the change in *E.M.F.* which is brought about by transformation of the electrolytic cadmium, a further change is found if the metal is deposited by passing a current through the above cell. This is due to the local transformation of the two-phase amalgam into a one-phase system. By diffusion of the cadmium, the two-phase equilibrium is, however, gradually restored, and the *E.M.F.* falls to its "normal" value after four or five days.

H. M. D.

**Atomic Weight of Lead of Radioactive Origin.** THEODORE W. RICHARDS and MAX E. LEMBERT (*J. Amer. Chem. Soc.*, 1914, 36, 1329—1344; *Compt. rend.*, 1914, 159, 248—250. Compare Soddy and Hyman, T., 1914, 105, 1402).—According to the views put forward by Russell, Fajans and Soddy (*A.*, 1913, ii, 274, 275, 276, 277), the nature of the end-product of the process of disintegration of a radioactive mineral will vary according to the proportion of the parent substances in the mineral. In order to test this theory, measurements have been made of the atomic weight of radioactive lead obtained from different sources.

The method adopted was very similar to that used by Baxter and Wilson (*A.*, 1908, ii, 281), which involves the preparation and analysis of the chloride of the metal. The results obtained show that all the radioactive specimens of lead examined by the authors have a lower atomic weight than ordinary lead. The actual values and the source of the lead are indicated in the following summary: lead from uraninite (North Carolina), 206.40; from pitchblende (Jachimsthal), 206.57; from carnotite (Colorado), 206.59; from Ceylonese thorianite, 206.82; from English pitchblende, 206.86; ordinary lead, 207.15.

The fact that all analyses were carried out by the same method, and that each sample gave consistent results, excludes the possibility of analytical error, and the authors consider that the variability indicated by the above atomic-weight numbers is definitely established. A similar result was also obtained by Soddy and Hyman in the determination of the atomic weight of lead from Ceylon thorite (*loc. cit.*).

The ultra-violet spectrum of a typical radioactive lead was found to be practically identical with that of ordinary lead. It would seem, therefore, that the admixed substance cannot be identified by spectroscopic or by chemical methods.

H. M. D.

**Atomic Weight of Lead from Pitchblende.** O. HÖNIGSCHMID and (Mlle.) St. HOROVITZ (*Compt. rend.*, 1914, 158, 1796—1798. Compare Curie, this vol., ii, 563).—The results of atomic-weight determinations of lead, using lead chloride obtained from pitchblende residues and carefully purified, give the value 206.736 as

the atomic weight of lead, this being the mean of nine determinations by Baxter's method. This low value is in accord with the view that radium by the loss of five  $\alpha$ -particles passes into radium-G, an element inseparable by chemical methods from lead, but possessing a different atomic weight, the value for which, calculated theoretically from those of uranium and radium, should be 205.62.

W. G.

**Cause of the Oxidation of Type Metal.** S. ZINBERG (*Zeitsch. angew. Chem.*, 1914, 27, 436—437).—The formation of lead hydroxide and carbonate on the surface of type metal is due to the action of moisture in the atmosphere. Whilst distilled water readily attacks an alloy containing 82% of lead and 14% of antimony, it has no action on one containing 72% of lead and 24% of antimony. The presence of certain salts in water, such as those contained in drinking water, inhibits the action of the latter on the metal, and this water may be employed for cleaning type metal, but the use of turpentine or petroleum is to be preferred for the purpose.

W. P. S.

**Experiments on White Lead.** R. STUART OWENS (*J. Physical Chem.*, 1914, 18, 461—473).—Experiments have been carried out on the production of white lead, lead carbonate, and lead hydroxide with the object of ascertaining how the physical properties of these substances change with the conditions of precipitation. It is shown that lead hydroxide can be precipitated in a definite crystalline form, and by varying the conditions the size of the crystals can be varied between  $1 \times 10^{-3}$  and  $37.5 \times 10^{-3}$  mm. in diameter. Lead carbonate is not precipitated in any definite crystalline form. It is probable that the particles are aggregates of very small crystals; the size of the particles can be varied between  $1 \times 10^{-3}$  and  $3.7 \times 10^{-3}$  mm. in diameter. When a mixture of particles of lead carbonate and lead hydroxide is kept under a solution of sodium acetate, particles of white lead are formed which have a uniform size, no matter what the size of the particles of the reacting substances. When a mixture of sodium hydroxide and sodium carbonate solutions is added to a solution of lead acetate, white lead is precipitated, and the size of the particles can only be varied between narrow limits ( $0.2 \times 10^{-3}$ — $2.0 \times 10^{-3}$  mm.). White lead prepared in this way does not show any definite crystalline form, but seems to consist of rounded, translucent particles. Rapid precipitation gives smaller particles, and slow precipitation larger particles. The absorption of oil by white lead is greater with larger particles than with smaller particles. Paint made from small-particle white lead is superior to that made from large-particle white lead. Uniformity in the size of the particles is not necessarily an advantage in a paint.

J. F. S.

**Allotropy of Copper.** II. ERNST COHEN and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 60—62. Compare this vol., ii, 205).—Further observations indicate that the transi-

tion temperature  $71.7^{\circ}$  recorded in the previous paper is to some extent dependent on the previous thermal history of the metal. At  $69.5^{\circ}$  the volume was found to increase, and then to decrease in a further series of observations. This behaviour seems to show that the metal consists of more than two allotropic modifications.

H. M. D.

**The Oxidation and Reduction of Copper.** JACQUES JOANNIS (*Compt. rend.*, 1914, 158, 1801—1804. Compare Berger, this vol., ii, 564).—A study of the rate of oxidation of copper and reduction of its oxide at  $300^{\circ}$  under varying pressure. The copper used was prepared electrolytically, and was in the form of fine wire 1 mm. diameter. It was placed in a cylindrical tube, heated in an electric furnace, and connected through a stop-cock to a chamber fitted with a manometer and stop-cocks, through which hydrogen or oxygen could be introduced. The progress of the reactions was followed by means of the manometer readings. Pressure apparently plays no appreciable part in the oxidation of copper, but the coating of oxide formed considerably diminishes the velocity of oxidation, even if a fresh supply of oxygen is introduced. In the process of reduction, pressure has apparently no influence either, but in this case it is impossible to draw any definite conclusions, owing to the velocity of condensation of the water formed.

W. G.

**The Influence of Nickel on Some Copper-Aluminium Alloys.** A. A. READ and R. H. GREAVES (*J. Inst. Metals*, 1914, 11, 169—213).—The mechanical properties are chiefly considered. The corrodibility of alloys of copper and aluminium containing 5 and 10% Al is small when sea-water is used, and is still further reduced by the addition of nickel. In acids, the alloys containing nickel are more readily corroded than those from which it is absent.

C. H. D.

**Muntz Metal.** J. E. STEAD and H. G. A. STEDMAN (*J. Inst. Metals*, 1914, 11, 119—150. Compare Bengough and Hudson, A., 1908, ii, 186).—Muntz metal, the alloy containing about 60% of copper and 40% of zinc, is rendered most ductile by prolonged annealing at  $430^{\circ}$ . At this temperature the  $\beta$ -constituent almost completely disappears in the course of several months, the specimen then consisting almost entirely of  $\alpha$ , although without loss of zinc. There is no evidence that the  $\beta$  is resolved into  $\alpha$  and  $\gamma$  (compare Carpenter, A., 1912, ii, 764; 1913, ii, 138, 139). During heating in air, the copper is completely protected from oxidation, the scale consisting only of zinc oxide.

C. H. D.

**The Micro-chemistry of Corrosion. II. The  $\alpha$ -Alloys of Copper and Zinc.** SAMUEL WHYTE and CECIL H. DESCH (*J. Inst. Metals*, 1914, 11, 235—251. Compare this vol., ii, 367).—Using the method previously described, brass containing 70% of copper and 30% of zinc is slightly more corroded in the cast than in the

annealed state, owing to the presence of cores in the crystallites formed on solidification. When 1% of zinc is replaced by tin, the corrosion is at first stimulated, but is rapidly checked by the formation of an adherent layer of basic salts. A similar effect is produced by 2% of lead.

Spontaneous and electrically stimulated corrosion are completely similar, the first process in each case being one of dezincification, which proceeds along the boundaries of crystal grains and along twinning planes.

C. H. D.

**Reduction of the Oxides of Copper and Nickel by Hydrogen in the Presence of a Dehydrating Agent.** E. BERGER (*Compt. rend.*, 1914, 158, 1798—1801. Compare Sabatier and Espil, this vol., ii, 276).—The reduction of oxides of copper and nickel is very considerably accelerated by the presence of a dehydrating agent such as barium oxide. The curve showing the rate of reduction of copper oxide is continuous, whilst in the case of nickel oxide, NiO, there is a break, showing the intermediate formation of the oxide, Ni<sub>2</sub>O. In the case of nickel, completely reduced, absorption of hydrogen continues until at 209.5° in forty hours the metal has absorbed three hundred times its volume of the gas, and the absorption still continues.

W. G.

**Colloidal Cuprous Oxide.** C. PAAL and A. DEXHEIMER (*Ber.*, 1914, 47, 2195—2199. Compare Paal and Leuze, A., 1906, ii, 356).—If a colloidal solution of cupric oxide, prepared by the method of Paal and Leuze (*loc. cit.*) with either sodium protolabate or lysalbate, is treated with a solution of pure hydroxylamine, reduction, which is accelerated by heating, takes place, with the evolution of gas, and leads to the quantitative formation of colloidal cuprous oxide. From the hydrosol thus prepared, the solid, soluble hydrogel may be obtained when air is excluded to prevent oxidation. According as the hydroxylamine is used in the equivalent quantity, or in excess, the hydrosol and hydrogel show different stabilities towards atmospheric oxidation, the presence of excess of hydroxylamine making them much more stable.

The hydrosols are bright orange in colour in transmitted light, and have a yellowish-grey, milky appearance in reflected light.

T. S. P.

**Position of Cerium in the Periodic System and Complex Molybdates of Quadrivalent Cerium.** G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 805—812).—The constitution of the complex molybdates described in this paper is analogous to that of the complex molybdates of zirconium and thorium, and this fact supports the view that cerium occupies a place in the same group as these elements in the periodic system. The neutral ammonium cerimolybdate, (NH<sub>4</sub>)<sub>8</sub>[Ce(Mo<sub>2</sub>O<sub>7</sub>)<sub>6</sub>].8H<sub>2</sub>O, is a yellow, crystalline substance yielding yellow solutions, which are stable towards hydrogen peroxide, and give a precipitate with oxalic acid only after prolonged boiling. Acid aniline cerimolybdate is a yellow

substance, which becomes green in the light. *Acid ammonium cerimolybdate*,  $(\text{NH}_4)_6\text{H}_2[\text{Ce}(\text{Mo}_2\text{O}_7)_6]\cdot 10\text{H}_2\text{O}$ , is a pale yellow, crystalline substance. *Silver cerimolybdate*,  $\text{Ag}_8[\text{Ce}(\text{Mo}_2\text{O}_7)_6]$ , is an orange-yellow, crystalline substance.

R. V. S.

**The Separation of Yttrium from the Yttrium Earths. II.** H. C. HOLDEN and C. JAMES (*J. Amer. Chem. Soc.*, 1914, 36, 1418—1423. Compare this vol., ii, 370).—The most efficient method for the separation of yttrium from the yttrium earth metals has been found to be the method of fractional precipitation with sodium nitrite. The oxides are dissolved in nitric acid, the solution diluted and boiled, and a quantity of sodium nitrite is added sufficient to precipitate the required fraction of the rare earth material. The yttrium concentrates in the later fractions. This method gives a larger yield, a more rapid separation, and is less expensive than the phosphate or chromate method. The method is not very effective, however, for the separation of yttrium from terbium.

H. M. D.

**The Chemical or Physical Nature of Colloidal Hydrrous Aluminium Silicates.** R. GANS (*Centr. Min.*, 1914, 365—368. Compare this vol., ii, 469).—Further discussion and reply.

L. J. S.

**Some Physical Properties of Indium Tribromide in Water.** ADOLF HEYDWEILLER (*Zeitsch. anorg. Chem.*, 1914, 88, 103—107).—The electrical conductivity, density, specific heat, and refractive index for three hydrogen lines have been determined for solutions of indium tribromide in water.

C. H. D.

**Metallic Bromides. VIII.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1914, 49, 834—844. Compare A., 1913, ii, 692, 957; this vol., ii, 214, 379).—When heated, anhydrous manganese bromide decomposes, with liberation of bromine. The tetrahydrate softens at 70—80°, and melts to a transparent liquid at 110°; Kuznetsov (*J. Russ. Phys. Chem. Soc.*, 1897, 29, 288) gave m. p. 64.3°. It loses 2H<sub>2</sub>O in a thermostat at 40°, or more readily at 50°, and 3H<sub>2</sub>O at 80°; the fourth molecule of water is expelled at 120°. In a desiccator over sulphuric acid it loses 2H<sub>2</sub>O rapidly, and a further H<sub>2</sub>O very slowly; over calcium chloride it gives up only 2H<sub>2</sub>O. Over sulphuric acid at 40 or 20 mm. pressure, it loses 3H<sub>2</sub>O, the residual monohydrate becoming anhydrous in an oven at 116°. In a current of dry air at 41°, the tetrahydrate gives up 2H<sub>2</sub>O rapidly, and the third H<sub>2</sub>O slowly, the fourth molecule of water being expelled only at 99°. Elimination of 1H<sub>2</sub>O from the tetrahydrate, with formation of  $\text{MnBr}_2\cdot 3\text{H}_2\text{O}$ , has not been effected.

When heated, hexahydrated magnesium bromide melts, and then loses water and hydrogen bromide, the dry residue giving up bromine on further heating. Under no conditions of heating was loss of water without decomposition observed.

When heated in moist air, glucinum bromide decomposes accord-



ing to the equations  $\text{GlBr}_2 + \text{O} = \text{GIO} + \text{Br}_2$  and  $\text{GlBr}_2 + \text{H}_2\text{O} = 2\text{HBr} + \text{GIO}$ .

Zinc bromide forms anhydrous crystals, and boils unchanged, but when heated with iodine it readily gives up bromine.

When heated near its boiling point, anhydrous cadmium bromide sublimes and gives up bromine, much of the latter being obtained if iodine is present. Its vapour density was found to be 9.22 and 9.28, instead of 9.40, at 923° and 914° respectively.

Tetrahydrated cadmium bromide is completely dehydrated in a thermostat at 30°, or over sulphuric acid at 18–20°.

Mercuric bromide forms anhydrous crystals, and even when heated rapidly sublimes without liberation of bromine, but this does occur in presence of iodine. Bromine is not set free when the bromide is heated with 50% chromic acid solution, but is eliminated copiously in the presence of a saturated solution of chromium trioxide. Bromine is also lost when the bromide is shaken with potassium iodide solution and then heated with 50% chromic acid solution.

Anhydrous cuprous bromide readily evolves bromine when heated.

T. H. P.

**Manganese Sulphide and the Estimation of this Metal.** A. VILLIERS (*Compt. rend.*, 1914, 159, 67–69. Compare Raab and Wessely, A., 1903, ii, 697).—A study of the conditions governing the formation of the pink and green forms of manganese sulphide. Precipitation in a neutral solution saturated with ammonium and alkali salts gives a pink precipitate which does not turn green, whereas precipitation in a neutral solution containing but a small amount of foreign salts gives a pink sulphide, which slowly changes at the ordinary temperature into the green form. In order to obtain the green sulphide in the cold, any excess of acid should be first boiled off, the solution diluted, made alkaline with ammonia, and ammonium hydrogen sulphide added. For the estimation of manganese, the precipitation should always take place at 100° after the addition of ammonia in quantity sufficient to make the solution alkaline. By this means a very dense, green precipitate is obtained, which can be easily collected and washed.

W. G.

**Preparation of Hydrates of Manganese Sulphate.** R. DE FORCAND (*Compt. rend.*, 1914, 158, 1760–1763. Compare Cottrell, A., 1901, ii, 12, and Richards and Fraprie, A., 1901, ii, 553).—The author has prepared the heptahydrate, tetrahydrate, and what he considers to be two dihydrates, and two monohydrates of manganous sulphate, as well as two anhydrous salts. One series of hydrates was prepared in the cold, starting with the heptahydrate, and subjecting it to successive dehydration by efflorescence, the final stages being carried out in a vacuum over phosphoric oxide. The starting point of the second series was a cold saturated solution of the tetrahydrate, which was heated to 36° and evaporated by a current of air played on to the surface of the

liquid. No indication of a hexahydrate was obtained, and the formation of a trihydrate was uncertain. W. G.

**Thermochemical Study of Some Hydrates of Manganese Sulphates. Isomerides.** R. DE FORCRAND (*Compt. rend.*, 1914, 159, 12—16).—The author has determined the heats of solution at 15° of the hydrates of manganous sulphate prepared on the one hand in the cold, and on the other at 100° (compare preceding abstract). The results obtained for the series B, prepared at 100°, are in agreement with Thomsen's values for the anhydrous salt and the monohydrate, and for the pentahydrate prepared in series A, in the cold, the heat of solution agrees with that obtained by Thomsen. For the anhydrous salts and the mono-, di-, tri-, and tetra-hydrates of series A, there is a marked difference between their heats of solution and the values given by Thomsen, the difference increasing as dehydration proceeds. The author considers that the anhydrous salt and the hydrates used by Thomsen are polymerides of his salts of series A, the polymerisation being brought about by rise in temperature. This polymerisation is exothermic and irreversible. The difference between the values for the tetrahydrates of the two series is small, and the hypothesis suggested by the author is that on warming the tetrahydrate it loses water and undergoes progressive polymerisation, which reaches its maximum in the neighbourhood of the monohydrate, the final heating from 100° to 300° only serving to complete the dehydration. This polymerisation can be produced in the cold by the action of sulphuric acid as a catalyst on a saturated solution of the monohydrate obtained in series A. W. G.

**The Velocity of Transformation of Steels on Heating, and the Specific Electrical Resistance of Iron.** A. PORTEVIN (*Compt. rend.*, 1914, 159, 51—53).—For a given steel, heated to a given temperature and cooled under identical conditions, the amount of carbon entering into solid solution will depend only on the amount of carbon in solid solution at the commencement of rapid cooling, which is a function of the time of heating at the given temperature. The first value, which can be determined by measuring the electrical resistance of steel, thus affords a measure of the velocity of transformation on heating at a given temperature. The results obtained show that the entry of the carbon into solution is far from being instantaneous. The elevation of the temperature and the increase in the time of heating increase the electrical resistance of the tempered steel. The author finds by extrapolation the value 9.3 microhms at 20° for the resistance of pure iron. W. G.

**The Hardness and Electrical Resistance of Iron-Carbon Alloys.** RUDOLF VONDRÁČEK (*Intern. Zeitsch. Metallographie*, 1914, 6, 172—182).—The hardness of martensite is not to be attributed to the presence of finely divided cementite, which could not give rise to a hardness much greater than that of pearlite. The elec-

trical resistance of martensite is such that the whole of the carbide must be present in solid solution. Cold-working is without any considerable influence on the resistance of steel. The resistance figures indicate that  $\alpha$ -iron is capable of holding as much as 0.14% of carbon in solid solution from 600° downwards when very slowly cooled in presence of a large excess of cementite. The  $\alpha$ -iron present in the eutectoid (pearlite) contains 0.06–0.07% C. at the temperature of formation, increasing to 0.14% with falling temperature.

C. H. D.

**The Influence of Manganese on the Corrosion of Steel** CECIL H. DESCH and SAMUEL WHYTE (*J. West Scotland Iron Steel Inst.*, 1914, 21, 176–191).—The corrosion of steels containing manganese in 5% sodium chloride solution has been examined by the method previously described (this vol., ii, 367). A distinct influence of manganese has not been observed. Manganese is preferentially dissolved, the ratio of manganese to iron in the solution increasing to a maximum and then diminishing. The maximum is also marked by a reversal in the etching, ferrite being at first attacked more than pearlite, whilst the etching is normal after the maximum is passed.

C. H. D.

**Magnetic Study of Iron Sesquioxide.** RUBY WALLACE (*Compt. rend.*, 1914, 159, 49–51).—A study of the variation with temperature of the magnetic susceptibility of the three forms of ferric oxide prepared (1) by precipitation in the cold with ammonia from a freshly prepared, dilute solution of ferric chloride; (2) by boiling the previous form with water; (3) by the action of water on sodium ferrite. For form (1) the magnetic susceptibility at first increases with the temperature, reaching a maximum at 200°, diminishes rapidly to 300°, and then slowly to a minimum at 650°, above which temperature it slowly rises. The magnetic susceptibility of form (2) diminishes continually, there being a rapid fall at 200°, and at 350° its curve joins that of form (1). The curve for form (3) is analogous to that for form (1), its minimum being situated at 750°. To confirm the temperatures of final transformation, the author has made a thermal analysis of the oxides by means of the Le Chatelier-Saladin double galvanometer.

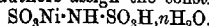
W. G.

**Bromination of Cobalt and Nickel in the Presence of Ethyl Ether.** F. DUCELLIEZ and A. RAYNAUD (*Compt. rend.*, 1914, 158, 2002–2003).—On bromination of cobalt or nickel in dry ether, according to the conditions given for manganese (compare this vol., ii, 273, 470), the bromine readily combines with the metal, giving the respective bromides, containing 1 mol. of ether, namely,  $\text{CoBr}_2 \cdot \text{Et}_2\text{O}$  and  $\text{NiBr}_2 \cdot \text{Et}_2\text{O}$ . The cobalt compound is green, and less stable than the nickel compound, which is yellow. Each of them on heating yields the anhydrous bromide.

W. G.

**Some Compounds of Univalent Nickel.** L. TSCHUGAEV and W. CHLOPIN (*Compt. rend.*, 1914, 159, 62–64. Compare Bellucci and Corelli, A., 1913, ii, 604; i, 839; this vol., i, 260).—On mixing

concentrated solutions of sodium hyposulphite and nitrite in molecular proportions, the resulting mixture gives with nickel salts of the type  $\text{NiX}_2$  a deep violet or blue coloration, according to the proportion of nickel used. The violet-coloured substance is more soluble than the blue. It has been isolated in a moderately pure state, and to it the authors assign the constitution



With alkali hydroxides it gives a blue precipitate, quite different in character from nickelous hydroxide, and at the same time ammonia is liberated and sodium sulphate formed. Potassium cyanide changes its violet colour to red. Ammonia, pyridine, and ethylenediamine give a deep blue coloration quite different from that obtained under the same conditions with nickelous salts. Ammonium hydrogen sulphide gives an amorphous, black precipitate soluble in potassium cyanide. The blue precipitate obtained with alkali hydroxides is shown to be the hydroxide  $\text{NiOH}$ , and with sodium sulphite it gives the subsulphide  $\text{Ni}_2\text{S}$ . The red coloration obtained with potassium cyanide is due to the formation of the complex cyanide obtained by Bellucci and Corelli (*loc. cit.*).

W. G.

**Colloidal Nickelous Hydroxide.** C. PAAL and GUSTAV BRÜNJS (*Ber.*, 1914, 47, 2200—2202).—Colloidal solutions of nickelous hydroxide are readily obtained from solutions of nickel sulphate by the ordinary methods involving the use of either sodium protalbate or sodium lysalbate, followed by dialysis. The solutions are clear in transmitted light, but in reflected light they are opalescent, with a greenish-yellow colour. Concentration in a vacuum gives brownish-yellow, transparent, brittle lamellæ, which dissolve again to the colloidal solution.

Sodium protalbate or lysalbate has only a slight protective action on colloidal solutions of nickelous hydroxide, so that solutions containing a high percentage of the colloid cannot be obtained.

T. S. P.

**Properties of Recoura's Green Chromium Sulphate.** ANDRÉ KLING, D. FLORENTIN, and P. HUCHET (*Compt. rend.*, 1914, 159, 60—62).—Working with an  $N/2$ -solution of the green chromium sulphate, obtained by Recoura by heating the crystalline, violet sulphate to  $90^\circ$  (compare A., 1896, ii, 27), the authors have determined the variation with time of (a) the amount of sulphuric acid in the solution precipitable by benzidine hydrochloride; (b) the lowering of the freezing point of the solution; (c) the electrical conductivity of the solution. During the first twenty-four hours after the preparation of the solution no sulphate precipitate is obtainable, but after that time the amount increases at first rapidly, and then gradually with passage of time. The molecular lowering of the freezing point and the electrical conductivity at first increase rapidly, even before the presence of the  $\text{SO}_4^{=}$  ion can be detected, and then attain a value which remains almost constant during the rest of the experiment. The green solutions

of chromium sulphate tend towards a state of equilibrium, which is a function of the temperature and concentration, and is the state towards which the violet solutions of the same concentration gradually pass.

W. G.

**Transformation Phenomena in Potassium Molybdates and Tungstates.** II. M. AMADORI (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 800—805. Compare this vol., ii, 568).—Potassium molybdate is trimorphous, and has a transformation point at about  $460^{\circ}$ . The second transformation point is observed at  $322\text{--}326^{\circ}$  during heating; the thermal effects observed during cooling are of no value, because the substance shows a great tendency to remain in an unstable state in the form stable at higher temperatures. Potassium tungstate is also trimorphous with a transformation point at about  $600^{\circ}$  and a second transformation point (observable only during heating) at  $370\text{--}374^{\circ}$ . To results obtained by cooling the same objections apply as in the case of potassium molybdate. R. V. S.

**Revision of the Atomic Weight of Uranium.** O. HÖNIGSCHMID (*Compt. rend.*, 1914, 158, 2004—2005).—The author has determined the atomic weight of uranium from the ratio  $\text{UBr}_4 : \text{AgBr}$ , and finds the value 238.175. The uranium bromide was prepared by heating a mixture of uranium oxide and carbon in bromine vapour, subliming the product, melting it, and transferring it to a silica weighing tube, the whole process being carried out in a silica apparatus in the absence of air. In one series of determinations the sublimation was performed in bromine vapour, and in the other in nitrogen. The oxide used was prepared from a pure specimen of uranyl nitrate, and carefully purified by repeating the process.

W. G.

**Vanadium in Brass.** R. J. DUNN and O. F. HUDSON (*J. Inst. Metals*, 1914, 11, 151—168).—The critical point at about  $460^{\circ}$  in alloys of copper and zinc containing the  $\beta$ -phase is only slightly affected by vanadium, 1% only raising it about  $10^{\circ}$ . Vanadium is practically without influence on the resolution of the  $\beta$ -phase. Alloys containing more than 0.5% V contain hard, blue inclusions, possibly an oxide.

C. H. D.

**Preparation of Solutions of Colloidal Vanadic Acid from Orthovanadic Esters.** J. D. RIEDEL, A.-G. (*Chem. Zentr.*, 1914, i, 1738; from *Riedel's Bericht.*, 1914, 13—14. Compare Prandl and Hess, A., 1913, i, 815).—*iso*-Amyl orthovanadate,  $(\text{C}_5\text{H}_{11})_2\text{VO}_6$ , b. p.  $161^{\circ}/19$  mm., forms the most convenient starting point for the preparation of solutions of colloidal vanadic acid, which are free not only from foreign electrolytes, but also from any considerable quantity of alcohols or alcoholic derivatives. The ester (50 grams) is gradually added to boiling water (1 litre), and ebullition is continued until a homogeneous dark red solution is obtained. After cooling, the amylene hydrate is extracted with ether, and the latter removed by passing a current of air through the

boiling solution. In the deep red solution about 7.99% of the vanadic acid is dissolved in the non-colloidal form, which, however, is only dissociated to a slight extent.

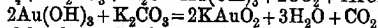
H. W.

**Chemistry of Gold. II. Auto-reduction as a Factor in the Precipitation of Metallic Gold.** VICTOR LÄNNER (*J. Amer. Chem. Soc.*, 1914, 36, 1423—1426. Compare A., 1913, ii, 614).—Reference is made to the precipitation of metallic gold from aqueous solution by the action of oxidising agents, the action being supposed to consist in auto-reduction. In particular attention is called to the activity of manganese compounds and the geological importance of auto-reduction as a factor in the secondary deposition of gold.

H. M. D.

**The Reaction in the Preparation of Colloidal Gold Solutions by the Formaldehyde Method, and the Influence of Carbon Dioxide on the Formation of these Solutions.** W. NAUKOV (*Zeitsch. anorg. Chem.*, 1914, 88, 38—48).—The production of a red colloidal solution of gold by Zsigmondy's method (A., 1898, ii, 522) is prevented by the presence of carbonic acid. The colloidal solution may also be prepared by Menz's method if carbon dioxide is removed by boiling (A., 1909, i, 133). A red colloidal solution once prepared, however, is not altered by passing a stream of carbon dioxide through it.

The potassium carbonate in the preparation may be replaced by potassium hydroxide. The first reaction is the formation of gold hydroxide, which is then converted into an aurate. The equations  $\text{HAuCl}_4 + 2\text{K}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Au}(\text{OH})_3 + 2\text{CO}_2 + 4\text{KCl}$  and



are confirmed by determinations of the quantity of carbon dioxide evolved.

Stable, red solutions may also be prepared by reducing potassium aurate with formaldehyde.

C. H. D.

**Platinum.** A. GUTHEIM, F. KRAUSS, and L. VON MÜLLER (*Chem. Zentr.*, 1914, i, 1162; from *Sitzungsber. physikal.-med. Sozi. Erlangen*, 45, 25—30).—In continuation of the previous work on substituted ammonium platinibromides (A., 1911, i, 32), the authors have investigated the corresponding alkali salts. Preparation is effected by addition of a solution of the pure alkali bromide to an aqueous solution of hydrogen platinibromide and crystallisation of the precipitates from dilute hydrobromic acid. The salts are thus readily purified, and crystallise in regular octahedra. The solubility in water and dilute hydrobromic acid decreases with increasing molecular weight. The solutions are red, and become pure yellow on dilution with water. They are readily decomposed by hydrazine hydrate with precipitation of platinum and evolution of nitrogen.

A deep carmine-red solution of pure hydrogen platinibromide is prepared by converting chemically pure platinum into the chloride, repeatedly evaporating this on the water-bath with highly concen-

trated hydrobromic acid, and then treating it similarly three or four times with hydrobromic acid containing bromine. The residue is dissolved in moderately dilute hydrobromic acid and filtered. Ammonium platinibromide,  $(\text{NH}_4)_2\text{PtBr}_6$ , is dark brown. The corresponding potassium and rubidium salts are dark brown and reddish-yellow respectively, and obstinately retain traces of water. The caesium salt is reddish-yellow. H. W.

### Mineralogical Chemistry.

Sulphur-containing Oil extracted from the Schists of Saint Champ. DEMESSE and RÉAUBOURG (*Bull. Soc. chim.*, 1914, [iv], 15, 625—627).—Analysis of this oil gave the following results: C=77.3, H=9.2, O(by difference)=1.14, N=0.37, S=11.99%. Sulphonation and neutralisation with ammonia convert it into a mixture of sulpho-derivatives similar to those employed therapeutically under various trade names. A. J. W.

Minerals from the Island of Nisiro (Ægean Sea). EMANUELE GRILL (*Mem. R. Accad. Lincei*, 1914, [v], 10, 14—23).—The specimens of sulphur, hæmatite, quartz, garnet, pyroxene (diopside), spinel, and calcite here described are, like the Island of Nisiro, of volcanic origin. Octahedral hæmatite was found in homogeneous crystals, which are of uniform specific gravity and consist wholly of ferric oxide; these crystals cannot, therefore, be pseudomorphs, as is probably the case with the martite from Brazil. T. H. P.

Minerals from the Pegmatites of Ambatofotsikely, Madagascar. L. DUPARC, R. SABOT, and M. WUNDER (*Bull. Soc. franç. Min.*, 1914, 37, 19—30).—Spessartite (analysis I) is formed as small, brownish-yellow, transparent fragments, and as inclusions in hæmatite. Gahnite (II) as greenish-black fragments with vitreous lustre and hardness 8; regarding some of the iron as ferrous, the formula is calculated as  $90.6(\text{Al}_2\text{O}_3, \text{ZnO}), 8.5(\text{Al}_2\text{O}_3, \text{FeO}), 0.9(\text{Fe}_2\text{O}_3, \text{MnO})$ . Ilmenite (III) as fragments with brownish-black colour and bluish-black streak; it is feebly radioactive. Red-ochre (IV), friable and compact; completely soluble in hydrochloric acid except a small, black residue. Zircon (V), a large, dark brown crystal ( $8 \times 4$  cm.). Hæmatite (VI) occurs as large plates in schists at Betaimby, prov. Mevatanana, and is remarkable in being strongly magnetic. The laterites derived from these schists are washed for gold and platinum metals, and hæmatite, together with magnetite, forms the bulk of the black residual sands. The hæmatite and magnetite were examined for gold and platinum, but with negative results:

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	Total	Sp. gr.
I.	86.31	—	20.39	1.26	15.02	25.24	0.83	0.15	99.20	4.1577
II.*	—	—	54.92	4.80	—	0.33	—	—	99.91	4.6094
III.†	0.16	51.32	—	2.10	42.38	3.37	—	—	100.53	4.7106
IV.‡	1.95	0.14	2.66	86.50	1.41	—	—	—	100.46	4.1693
V.‡	28.45	—	—	0.05	—	0.18	—	—	100.48	4.5834
VI.	0.25	0.83	—	99.63	0.63	trace	—	trace	101.34	5.1726

\* Also ZnO, 39.86.

† Also U<sub>3</sub>O<sub>8</sub>, 0.20.

‡ Also ZnO, 71.80.

§ Also lost on ignition, 7.80.

L. J. S.

**Lubinitze, the Monoclinic Modification of Calcium Carbonate.** RICHARD LANG (*Jahrb. Min. Beil. Bd.*, 1914, 38, 121—184).—"Rock-milk" of a milk-white colour and with a texture resembling that of mould or cotton-wool occurs as a coating in crevices in the calcareous tufa of the Diessen valley, near Horb, in Württemberg. Under the microscope it is seen to consist of a mass of minute, capillary crystals, which are determined as monoclinic with refractive indices,  $\alpha=1.48$ ,  $\beta=1.54$ , and  $\gamma=1.66$  approximately. It has  $D=2.65$ , and the material acquires a lilac colour after treatment for about twenty minutes with cobalt nitrate solution. The following analysis shows the material to be anhydrous calcium carbonate:

CaO.	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>	MgO.	Loss at 100°.	Loss on ignition.	Total.
55.60	0.19	0.15	0.10	0.04	44.02	100.14

A detailed review is given of the literature relating to the different forms of calcium carbonate (compare A., 1909, ii, 492; 1911, ii, 121), and of their different behaviour with colouring reagents. The modifications recognised are: bütschliite (amorphous), calcite (rhombohedral), aragonite (orthorhombic), vaterite (feebly birefringent), and lubinitze (monoclinic).

L. J. S.

**Barthite, a Zinc Copper Arsenate from German South-West Africa.** M. HENGLEIN and W. MEIGEN (*Centr. Min.*, 1914, 353—355).—This new mineral occurs as grass-green, crystalline crusts or quartz crystals in cavities in red dolomite from Guchab, in the Otavi valley. The crystals are optically biaxial, and probably monoclinic.  $D_{14} 4.19$ ; hardness 3. The following analysis gives the formula:  $3\text{ZnO} \cdot \text{CuO} \cdot 3\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , or, written as a meta-arsenate,  $3\text{Zn}(\text{AsO}_3)_2 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , showing the mineral to be distinct from veselyite:

CuO.	ZnO.	As <sub>2</sub> O <sub>5</sub>	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O.	Insol.	Total.
8.5	23.3	64.0	1.0	3.2	1.1	101.1

L. J. S.

**Augite from Bail Hill, Dumfriesshire.** ALEXANDER SCOTT (*Min. Mag.*, 1914, 17, 100—110).—Sharply developed crystals of black augite are found loosely embedded in andesitic tuffs at this locality. The crystals are simple or twinned, and show a peculiar curvature of the faces, and also "hour-glass" and zonal structures. The different sectors of the crystals show differences in optical



characters (refractive indices are given), and no doubt they differ in chemical composition, probably in the relative amounts of titanium dioxide present, since this "hour-glass" structure is typical of titanagites. It was, however, found impracticable to separate the sectors for analysis; a bulk analysis of the crystals gave:

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO
45.66	2.16	3.53	8.78	4.16	0.19	9.34	22.17
Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O > 110°	H <sub>2</sub> O < 110°	P <sub>2</sub> O <sub>5</sub>	Total	Sp. gr.	
1.50	0.28	1.37	0.61	trace	99.73	3.291	

L. J. S.

**Prehnite from Baffin Land, Arctic Canada.** ROBT. A. A. JOHNSTON (*Victoria Memorial Museum, Geol. Survey, Canada, Bull. No. 1*, 1913, 95—98).—Pale green, translucent prehnite intimately intermixed with calcite and quartz forms small veins in shale near igneous intrusives at Adams Sound on Admiralty Inlet. Analysis of material separated as far as possible from quartz gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	H <sub>2</sub> O	Total	Sp. gr.
44.35	19.44	6.58	25.50	4.00	99.87	2.924

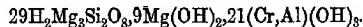
The excess of about 4.38% silica probably represents admixed quartz. On account of the high content of iron, this variety of the mineral is called *ferroprehnite*.

L. J. S.

**A New Alteration Product of Serpentine.** LAURA HEZNER (*Contr. Min.*, 1914, 386—388).—The material is an alteration product of a serpentine rich in chromite, and comes from Macedonia. In its lilac colour it resembles the Tasmanian mineral stichtite (of W. F. Petterd, 1910; compare A., 1912, ii, 1061), but it differs from this in being compact; under the microscope it is, however, seen to be scaly in texture. Analysis gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	H <sub>2</sub> O < 110°	H <sub>2</sub> O > 110°	CO <sub>2</sub>	Total
31.32	3.87	11.53	1.63	1.15	36.64	0.23	11.09	3.03	100.54

Deducting admixed carbonates and chromite, the formula suggested is:



L. J. S.

**Occurrence of Tourmaline in the Serpentine of the Urals.** L. DUPARC and H. SIGG (*Bull. Soc. franç. Min.*, 1914, 37, 14—19).—Radial aggregates of black needles and prisms of tourmaline occur embedded in serpentine near a limestone contact at Sewersky, in the Syssert mining district, southern Urals. The antigorite, of which this serpentine is normally composed, is here replaced by chlorite with biotite and in places large plates of muscovite, the

rock being, in fact, altered by the same pneumatolytic agents which gave rise to the tourmaline. Analysis of the tourmaline gave:

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO
33.72	2.52	29.19	4.99	5.14	0.40	1.70	7.97
Li <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	F	H <sub>2</sub> O	Total	
traces	0.22	1.04	8.73*	0.50	2.40	98.52	

\* Probably somewhat low.

L. J. S.

The Mineralogical Constitution of the Shetlands of the South. E. GOURDON (*Compt. rend.*, 1914, 158, 1905—1907. Compare *ibid.*, 1914, 158, 583).—The author has made a mineralogical study of Bridgman Island, Deception Island, and Admiralty Bay in the South American Antarctic. Analyses of the following rocks have been made, and the results are quoted: (a) trachy-andesite from Deception Island; (b) the same; (c) andesite with hypersthene from Admiralty Bay; (d) andesite from Deception Island; (e) labradorite from Deception Island; (f) doleritic basalt from Deception Island; (g) labradorite with olivine from Bridgman Island:

	a.	b.	c.	d.	e.	f.	g.
SiO <sub>2</sub> .....	69.01	67.71	57.80	80.62	53.50	49.84	54.24
Al <sub>2</sub> O <sub>3</sub> .....	14.21	14.65	17.87	16.22	17.62	19.37	17.20
Fe <sub>2</sub> O <sub>3</sub> .....	2.23	1.59	2.17	1.76	2.58	3.42	2.81
FeO .....	2.89	3.29	3.79	5.67	6.07	3.69	4.98
MgO .....	0.62	0.85	2.57	1.62	4.39	4.71	5.84
CaO .....	2.11	2.34	6.72	4.18	9.22	12.35	10.19
Na <sub>2</sub> O .....	6.30	6.09	3.25	6.25	4.15	2.50	2.91
K <sub>2</sub> O .....	2.07	1.99	0.96	1.20	0.75	0.87	0.92
TiO <sub>2</sub> .....	0.58	1.00	0.56	1.54	1.65	1.32	0.91
P <sub>2</sub> O <sub>5</sub> .....	0.12	0.16	0.20	0.24	0.36	0.11	0.09
H <sub>2</sub> O .....	0.09	0.16	4.26	0.56	0.00	1.79	0.09
	100.23	99.83	99.75	99.86	100.29	99.97	100.18

W. G.

Optically Uniaxial Augite from Mull. A. F. HALLIMOND with an analysis by E. G. RADLEY (*Min. Mag.*, 1914, 17, 97—99).—The mineral occurs as minute phenocrysts in a dark, glassy, magnetite-bearing rock near Pennygael. It is remarkable in being practically optically uniaxial,  $\omega = 1.714$ ,  $\epsilon = 1.744$  (Na); extinction-angle on the prism cleavages,  $30\frac{1}{2}^\circ$ . D<sub>57</sub> 3.44. Analysis gave:

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO
49.72	0.85	0.90	1.72	27.77	0.93	3.80
MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Li <sub>2</sub> O	H <sub>2</sub> O at 105°.	H <sub>2</sub> O > 105°.	Total
12.69	0.12	0.23	trace	0.08	1.27	100.18

L. J. S.

Ægirite and Babingtonite. SILVIA HILLEBRAND (*Tsch. Min. Mit.*, 1913, 32, 247—264).—Analysis of a pure crystal of ægirite (containing not more than about 0.01% impurities) from Brevig, Norway, gave I, corresponding with a mixture of the molecules

$\text{NaFe}^{II}\text{Si}_2\text{O}_6$  (84.0%),  $\text{CaFe}^{II}\text{Si}_2\text{O}_6$  (7.3%),  $\text{CaMnSi}_2\text{O}_6$  (4.0%),  $\text{NaAlSi}_2\text{O}_6$  (3.5%), and  $\text{NaFe}^{II}\text{Ti}_2\text{O}_6$  (1.2%):

	$\text{SiO}_2$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$	Total	Sp. gr
I.	51.08	0.66	0.80	29.30	2.29	1.11	2.54	trace	11.50	1.04	100.32	3.558
II.*	52.57	—	—	15.03	6.61	6.62	19.85	trace	—	—	100.68	3.551

\* Also traces of  $\text{K}_2\text{O}$ ,  $\text{Li}_2\text{O}$ .

Pure crystals of babingtonite from Arendal, Norway, gave II, corresponding with a mixture of the molecules  $\text{Ca}_2\text{Si}_3\text{O}_8$  (52.50%),  $\text{Mn}_2\text{Si}_3\text{O}_8$  (15%), and  $\text{Fe}^{II}\text{Fe}_2^{II}\text{Si}_3\text{O}_8$  (32%). The presence of the last of these molecules (analogous to anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) recalls the comparison made by Dauber in 1855 between the crystallographic constants of babingtonite and anorthite.

Both ægirite and babingtonite are only incompletely decomposed by hydrochloric acid acting during three months at  $60^\circ$ ; determinations of the composition of the silicic acid so isolated gave no very definite results.

L. J. S.

### Analytical Chemistry.

**Gas Analysis Apparatus.** G. WEMPE (*Chem. Zeit.*, 1914, 38, 794).—The measuring burette is connected at its upper end through a six-way tap with a series of absorption vessels; rubber connexions are not employed, all the joints being fused. The burette and absorption vessels are provided with jackets and the six-way tap with a mercury-seal; a device is fitted at the top of the gas reservoir for preventing mercury passing into the burette.

W. P. S.

**Manostat for Use in Gas Analysis.** HARVEY N. GILBERT (*J. Ind. Eng. Chem.*, 1914, 6, 585—586).—In the combustion of gases confined over mercury in a pipette, the level of the mercury may be kept constant by fixing the mercury reservoir on a support carried on two pivoted parallel arms fixed to a vertical rod; a coiled spring, suspended from the upper part of the rod, is attached to an adjustable point on the lower arm, so that the vertical distance through which the support and reservoir move can be regulated to balance the height of the column of mercury which has left the pipette.

W. P. S.

**The Preparation and Properties of "Lacmosol," the Sensitive Constituent of the Indicator, Lacmoid.** R. HORTINGER (*Biochem. Zeitsch.*, 1914, 65, 177—188).—The ordinary commercial preparations of lacmoid contain only about 20% of "lacmosol," which is the constituent to which the indicator owes its distinctive properties. This constituent can be prepared in the following way. Ten grams of resorcinol are heated with 2 c.c. of concentrated sodium nitrite solution for forty minutes at about  $105^\circ$  (but not above  $110^\circ$ ). The product is then thrown into at least one litre of concentrated sodium chloride solution acidified with hydrochloric acid. The precipitate, after washing with concen-

rated salt solution, is purified by dissolving in ammonia and reprecipitating with acid (in concentrated salt solution). This precipitate is then dissolved in a small quantity of acetone or alcohol, and the solution thus produced is thrown into about thirty times the volume of ether. The "lacosol" remains in solution, whereas the non-essential substances are precipitated. It is soluble in ether, and can be finally purified by extraction with this solvent in a Soxhlet apparatus. The turning point of the pure indicator is far sharper than that of the ordinary preparation. It possesses a violet colour at the  $[H^+]$  concentration  $1 \times 10^{-5}$ . S. B. S.

**Picric Acid for Standardisation Purposes.** OTTO PFEIFFER (*Zeitsch. angew. Chem.*, 1914, 27, 383).—The use of pure picric acid for the standardisation of iodine and acid and alkali solutions involves in the latter case, according to Sander's method (A., 1914, i. 482), the comparison of the picric acid solution with the mineral acid by means of a mixture of iodide and iodate, and a thiosulphate solution. Preferable to this indirect method is the standardisation of an alkali solution by direct titration with the picric acid, using dimethylaminoazobenzene as indicator. The alkali must be run into the picric acid solution, and an extremely delicate end-point is obtained by observing, not the colour of the whole solution, but the local brightening in colour which is produced by each drop of alkali solution as it falls, so long as the slightest trace of picric acid remains unneutralised. G. F. M.

**Detection of Halogens in Benzoic Acid.** E. WENDE (*Chem. Zentr.*, 1914, i, 1302; from *Apoth. Zeit.*, 1914, 29, 157).—A quantity of about 0.1 gram of the benzoic acid is heated with 0.5 gram of yellow mercury oxide; the mixture is then boiled with 10 c.c. of dilute nitric acid, filtered, and the filtrate is tested with silver nitrate solution. W. P. S.

**Effect of Ferric Salts and Nitrites on the  $\alpha$ -Tolidine and Starch-Iodide Tests for Free Chlorine.** J. W. ELLMS and S. J. HAUSER (*J. Ind. Eng. Chem.*, 1914, 6, 553–554. Compare this vol., i. 66).—The presence of ferric salts, nitrites, or any oxidising substance, interferes with these tests for free chlorine, the starch-iodide test being affected to the greater extent. In using the test care should be taken to ascertain that the coloration produced is due to chlorine, and not to other substances. W. P. S.

**Methods of Estimating Chlorine in Urine.** H. ROGÉE (*Chem. Zentr.*, 1914, i, 1221; from *Apoth. Zeit.*, 1914, 29, 150–151).—Of various methods examined, those described by Volhard and by Bang (estimation of the chlorine by Mohr's method after the removal of purine bases by blood charcoal) were found to be trustworthy. Mohr's method, however, yielded correct results only in the case of neutral albumin-free urines. Weisz's method, in which an apparatus called a chlorometer is used, gave low results. W. P. S.

**Detection of Iodine in Urine.** ERDMANN (*Chem. Zentr.*, 1914, i, 1221; from *Schweiz. Apoth. Zeit.*, 1914, 52, 93—94).—A method proposed by Losser, depending on the formation of yellow mercurous chloride when a urine containing iodine is treated with mercurous chloride, was found to be capable of detecting the presence of 0.01% of iodine in urine, but not 0.005%; the latter quantity, however, showed a distinct reaction when the urine was treated with chlorine water and chloroform. Barth's test for nitrates in milk (A., 1913, ii, 1069) fails in the case of milks which have been heated for a long time at 60° or higher. W. P. S.

**Physiology of the Thyroid. III. Additions to the Method of Iodine Estimation.** F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1914, 91, 392—399. Compare A., 1913, ii, 722).—Experience in the use of the method of estimating iodine in products of animal origin (*loc. cit.*) leads the authors to recommend certain procedure here described, especially in regard to the incineration of the material. R. V. S.

**Blacher's Method of Estimating the Hardness of Water.** JULIUS ZINK and FRIEDRICH HOLLANDT (*Zeitsch. angew. Chem.*, 1914, 27, 437—440. Compare A., 1908, ii, 897; 1913, ii, 982).—This method was found to be trustworthy for the estimation of hardness, and also of sulphates, in water. W. P. S.

**Disturbing Effect of Colloids in the Determination of Hardness by Clark's Method.** J. D. RUVS (*Chem. Weekblad*, 1914, 11, 599—602).—Determinations of the hardness of water containing gelatin have proved that 5—10 milligrams of this substance per litre lower the apparent hardness by about 2.5°, and 10—25 milligrams by about 7.5°. The author considers that the presence of colloids renders Clark's method wholly untrustworthy. A. J. W.

**Improvement of the Barium Sulphate Estimation of Sulphur in Soluble Sulphates when Sodium Salts are Present.** W. A. TURNER (*Amer. J. Sci.*, 1914, [iv], 38, 41—44).—The effect of sodium salts on the precipitation of barium sulphate may be eliminated by carrying out the estimation as follows: The substance, equivalent to about 1 gram of barium sulphate, is dissolved (after fusion, if necessary, with sodium carbonate and sodium peroxide) in a small quantity of water, and the solution is treated with five times its volume of concentrated hydrochloric acid. The precipitated sodium chloride is collected on an asbestos filter, washed with hydrochloric acid, and the filtrate evaporated to dryness after the addition of water. The residue is dissolved in water, 1 c.c. of 4% hydrochloric acid is added, the solution filtered, diluted to 350 c.c., heated to boiling, and a slight excess of barium chloride is added. The mixture is placed on a water-bath for some hours, and the barium sulphate is then collected and ignited at a low red heat. W. P. S.

**A Volumetric Method for the Estimation of Total Sulphur in Urine.** G. W. RAIZISS and H. DUBIN (*J. Biol. Chem.*, 1914, 18, 297—303).—The method proposed by the authors is a modification of one put forward by Benedict (A., 1909, ii, 827; compare also Rosenheim and Drummond, this vol., ii, 485). After oxidation, the sulphur is precipitated as benzidine sulphate, and the benzidine in this is estimated by titration with potassium permanganate in warm acid solution. The time required for the carrying out of the new method is very much less than what is required by the original Benedict process, and it has the further advantage that much smaller amounts of sulphur may be accurately estimated.

H. W. B.

**Volumetric Estimation of Sulphates.** HORACE NORTH (*Amer. J. Pharm.*, 1914, 86, 249—256).—A modification of Hinman's barium chromate method, which enables the process to be used in the presence of the ions Li, Na, K,  $\text{NH}_4$ , Cu, Mg, Ca, Sr, Zn, Cd, Hg, Al, Ni, Co, Cl,  $\text{PO}_4$  (little),  $\text{B}_2\text{O}_3$ . Iron and chromium should be absent. The solution (about 0.16 gram of  $\text{SO}_4$ ) is placed in a 100 c.c. flask, diluted to 30 c.c., and sufficient hydrochloric acid (D 1.12) is added to have 4 c.c. of free acid present. The liquid is heated to boiling, and 20 c.c. of  $N/3$ -barium chloride are added; then, after again heating to boiling, 10 c.c. of  $N$ -potassium dichromate. After rinsing the neck with 10 c.c. of water a mixture of 15 c.c. ammonia (D 0.98) and 2 c.c. of 36% acetic acid is added drop by drop with constant shaking. After cooling, the whole is made up to the mark, and, after filtering through asbestos, 40 c.c. are titrated iodometrically for chromic acid with  $N/10$ -thiosulphate as usual. The difference in chromic acid found between this result and that of an experiment without addition of sulphate represents the sulphuric acid.

L. DE K.

**New Method of Estimating Thiosulphate and Sulphite in Presence of One Another and also Aluminium and Glucinum.** V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 419—427).—The method recommended by Bodnár (this vol., ii, 67) for estimating thiosulphate and sulphite, when present together, gives good results only with very small proportions of thiosulphate. The method now proposed by the author is based on the varying oxidisability of the two kinds of salts, and exhibits an accuracy of 0.25—1%.

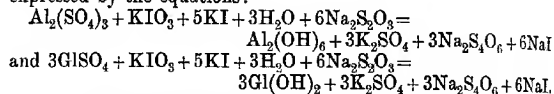
No oxidation of sodium thiosulphate occurs when its solutions are boiled for five minutes, and a current of air passed through for fifteen minutes, whereas sodium sulphite is practically completely oxidised (99%) under these conditions. In the presence of even small proportions of thiosulphate, however, the oxidation of sulphite is very considerably retarded. The author therefore uses potassium iodate as oxidising agent, the procedure being as follows.

An exact weight of 5—10 grams of the mixture is dissolved in water, and the solution carefully neutralised with 1% sodium carbonate solution and made up to 500 c.c. Of this liquid 20 c.c. are measured into each of two Erlenmeyer flasks of 250—300 c.c.

capacity, one portion being mixed with 100 c.c. of water and titrated directly with *N*/10-iodine solution in presence of starch. The second portion is mixed with 100 c.c. of water, 10 c.c. of 3% potassium iodate solution, and 10 c.c. of 1% potassium iodide solution, the flask being then covered with a watch-glass and left overnight (seventeen hours), and the liquid titrated with *N*/10-iodine solution. The volume of iodine solution employed in the second case corresponds with the amount of thiosulphate present, whilst the difference between the volumes required in the two cases gives the amount of sulphite.

When the proportion of thiosulphate present is small, this method gives accurate results for the sulphite, but low results for the thiosulphate. It is therefore advisable to heat 20 c.c. of the liquid, diluted as described above, on the water-bath for half an hour, and to titrate the cooled liquid with *N*/10-iodine solution. If the amount of the latter required does not exceed 0.5 c.c., the author's method for estimating the thiosulphate should be replaced by that of Bodnár (*loc. cit.*).

Experiment shows that the hydrolysis of aluminium and glucinum salts proceeds in presence of thiosulphate, and a method for estimating these salts has been devised in accordance with the reactions expressed by the equations:



A weight of the substance containing not more than 1.5 grams of  $\text{Al}_2\text{O}_3$  is dissolved in water to 500 c.c. To 10 c.c. of this solution, placed in a 250–300 c.c. Erlenmeyer flask, are added 100 c.c. of water, a mixture of 10 c.c. 3% potassium iodate solution, and 10 c.c. 1% potassium iodide solution, and, from a burette, 40 c.c. of *N*/10-sodium thiosulphate solution. The flask is covered with a watch-glass, and the liquid boiled for not more than five minutes; the excess of thiosulphate in the cooled liquid is then estimated by titration with *N*/10-iodine solution; 1 c.c. of the latter corresponds with 0.001704 gram  $\text{Al}_2\text{O}_3$  or 0.001255 gram  $\text{GIO}$ . Tests made with alum and with glucinum sulphate show that the method gives satisfactory results. When this method is applied to the analysis of clay containing free acid and admixtures, such as compounds of zinc and iron, these should be estimated and the proportion of alumina found suitably corrected: 1 c.c. of *N*/10-iodine solution corresponds with 0.002661 gram  $\text{Fe}_2\text{O}_3$ , 0.003592 gram  $\text{FeO}$ , 0.005086 gram  $\text{ZnO}$ , 0.001703 gram  $\text{NH}_3$ , or 0.004905 gram  $\text{H}_2\text{SO}_4$ .  
T. H. P.

**Detection of Very Small Quantities of Selenious Acid in Sulphuric Acid.** ERNST SCHMIDT (*Arch. Pharm.*, 1914, 252, 161–165).—Concentrated sulphuric acid containing about 0.25% of selenious acid has long been recommended as an alkaloidal reagent, particularly for morphine and codeine, with each of which it yields a blue and finally an olive-green coloration. Meyer and

Jannek (A., 1913, ii, 788) and Meyer and von Garn (this vol., ii, 67) describe methods whereby the presence of 0.002% of selenium dioxide can be detected, but the following process will detect 0.0005% of selenious acid. One c.c. of 0.1% aqueous selenious acid is mixed with 200 c.c. of pure sulphuric acid; 10 c.c. of the mixture and 0.01 gram of codeine phosphate produce a distinct green coloration after one minute, and a bluish-green coloration after fifteen minutes. Even 1 c.c. of the mixture produces the same colour phenomena. When the dilution of the selenious acid is diminished to 0.0001% the colour reactions can be observed with sufficient sharpness against a white surface, and in comparison with a solution of about 0.01 gram of codeine phosphate in 10 c.c. of pure sulphuric acid. The preceding process is not applicable when the sulphuric acid contains iron (for example, 1 drop of ferric chloride in 10 c.c. of sulphuric acid), but is not influenced by sulphurous acid, and is only retarded, not vitiated, by the presence of tellurous acid.

C. S.

**Estimation of Nitrogen in Guncotton by means of the Nitrometer.** E. G. BECKETT (*J. Soc. Chem. Ind.*, 1914, 33, 628—631).—The ordinary nitrometer method of estimating nitrogen in guncotton (shaking with sulphuric acid and mercury) yields trustworthy results. The 111—115 c.c. of gas evolved from 0.51 gram of guncotton contain about 0.4 c.c. of carbon dioxide plus sulphur dioxide, 0.3 c.c. of carbon monoxide, and 0.6 c.c. of nitrogen; the residual sulphuric acid contains nitrogen equivalent to 0.75 c.c. of nitric oxide. The 15 c.c. of 96.5% sulphuric acid employed were found to contain about 0.4 c.c. of nitrogen gas, of which 0.35 c.c. was evolved during the estimation. The errors introduced by these impurities thus balance one another. A modified method sometimes employed, in which 1 c.c. of water is added to the 15 c.c. of sulphuric acid, gives slightly higher results than the above method, the increase in the volume of gas evolved being caused by the presence of a larger quantity of carbon dioxide plus carbon monoxide plus sulphur dioxide in the nitric oxide, and is due to the heat produced by the addition of the water to the sulphuric acid, and not to the use of more dilute acid. W. P. S.

**Estimation of Nitrogen in Norwegian Saltpetre.** N. BUSVOLD (*Chem. Zeit.*, 1914, 38, 799—800).—The method recommended consists in reducing the nitrate with Devarda's alloy in alkaline solution, and estimating the resulting ammonia by distillation. A current of air is drawn through the apparatus (distillation flask, condenser, and receiver) during the distillation, and towards the end of the operation the flame is removed, the apparatus is closed, and allowed to cool. A low pressure is thus produced, and air is then again admitted and the distillation continued for a short time. Owing to the hygroscopic properties of calcium nitrate, a large quantity of the sample should be weighed out, dissolved in a definite volume of water, and portions of this solution used for the estimation.

W. P. S.



**The Evolution of Nitrogen in the Action of Sodium Hypobromite on Carbamide in a Vacuum.** O. ALBERTO GARCIA (*Bull. Soc. chim.*, 1914, [iv], 15, 574—575).—Working with solutions of carbamide of varying concentrations the author has obtained, in all cases, almost the theoretical quantity of nitrogen evolved by the action of sodium hypobromite, provided that the reaction took place in a vacuum. He explains the low results usually obtained by this method as due to solution of a portion of the nitrogen in the water used as solvent. W. G.

**Estimation of Amino-Acid- and Polypeptide-Nitrogen in Barley, Malt, and Beer.** LUDWIG ADLER [with RUCKDESCHKE] (*Chem. Zentr.*, 1914, i, 1529; from *Zeitsch. ges. Brauereien*, 1914, 37, 105—108, 117—121, 129—133).—Sørensen's formaldehyde method (A., 1908, i, 115) was found to be trustworthy for the estimation of amino-acids and polypeptides in materials used in brewing; it affords a means of ascertaining the protein decomposition reactions taking place during germination and mashing of the malt. The amount of pre-formed amino-substances in malt is about 38.5% of the quantity of total soluble nitrogen; this amount increases when the malt is steeped in water. W. P. S.

**Estimation of Protein-ammonia in Water.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1914, 27, 440).—One hundred c.c. of the water are acidified with 1 drop of concentrated sulphuric acid, about 0.06 gram of potassium persulphate is added, the solution is heated on a water-bath for fifteen minutes, cooled, and treated with 5 c.c. of a mixture consisting of equal volumes of Nessler's reagent and sodium potassium tartrate solution. The coloration obtained is compared with that produced by adding a definite quantity of ammonium chloride to 100 c.c. of the water previously treated with 1 drop of sulphuric acid, 0.05 gram of potassium persulphate, and 5 c.c. of the mixed reagent. W. P. S.

**Availability of Nitrogen in Kelp.** JOHN A. CULLEN (*J. Ind. Eng. Chem.*, 1914, 6, 581—582).—In the estimation of available nitrogen in kelp trustworthy results are obtained by the alkaline permanganate method only when a quantity of the latter is employed sufficient to oxidise the whole of the organic matter present. W. P. S.

**Reactions of Nitrates with Formic Acid and the Analysis of Nitrates.** UGO MOLINARI (*Chem. Zentr.*, 1914, i, 1221—1222; from *Staz. sperim. agrar. ital.*, 1913, 47, 24—32).—The method proposed by Quartaroli (A., 1911, ii, 1085) yields the best results when 95% formic acid is used for the decomposition of nitrates and when the reaction takes place in a Schiff's nitrometer, but in no case are the results trustworthy; the results obtained with potassium nitrate are from 91.33 to 94.55% of the quantity present, and with barium nitrate from 89.97 to 92.72%. The reaction does not proceed strictly according to the equation given by Quartaroli

(*loc. cit.*); a quantity of nitric oxide is always formed, and the yield of this gas, and of the nitrous oxide and carbon dioxide, varies with the conditions of the experiment.

W. P. S.

**The Factor for Calculation of the Phosphorus Content when Estimated by Neumann's Method.** WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1914, 64, 393—400).—In calculating the phosphorus content in analyses carried out by Neumann's method (A., 1903, ii, 243; 1905, ii, 68) it was found that the better results were obtained when 1 c.c. of *N*/2-sodium hydroxide was regarded as the equivalent of 0.565 mg. of phosphorus instead of the theoretically calculated quantity 0.553.

S. B. S.

**Estimation of Phosphorus in Biological Material.** A. E. TAYLOR and C. W. MILLER (*J. Biol. Chem.*, 1914, 18, 215—224).—For the estimation of comparatively large quantities of phosphorus, such as occur in urine, a modification of Neumann's method is described, in which the ammonium phosphomolybdate precipitate is washed with alcohol by centrifugalisation before being dissolved in *N*/2-alkali.

Minute amounts of phosphorus of the order of 0.0002 to 0.0010 gram are best estimated by a new colorimetric method depending on the colour produced on reducing the phosphomolybdate first formed with phenylhydrazine. For details, the original paper must be consulted. With this method the authors have found that blood serum contains from 0.004 to 0.006 gram of phosphorus in lipoidal combination per 100 c.c. of serum.

H. W. B.

**Detection of Phosphorus in Bones.** K. WÖRNER (*Chem. Zentr.*, 1914, i, 1605; from *Zeitsch. physikal. chem. Unterr.*, 1914, 27, 106).—The powdered bone is heated in a porcelain crucible with one-third of its weight of magnesium powder, and the resulting phosphide is detected by the liberation of phosphine when the mixture is treated with water.

W. P. S.

**Estimation of Inorganic Phosphoric Acid in the Presence of the Esters of Phosphoric Acid.** WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1914, 64, 401—408).—Inorganic phosphoric acid can be precipitated as ammonium phosphomolybdate of normal composition in the presence of 4% by volume of sulphuric acid and 15% ammonium nitrate within six hours at 37°. Small concentrations of phytin do not interfere with the precipitation, whereas large quantities do. Up to a six-fold excess of phytin phosphorus and a concentration of this of about 0.05%, it is possible to obtain not less than three-quarters of the total inorganic phosphorus by Neumann's method after a single precipitation. Glycerophosphoric acid influences the precipitation to a smaller degree than does phytin.

S. B. S.

**Preparation of Neutral Ammonium Citrate.** ERMON D. EASTMAN and JOEL H. HILDEBRAND (*J. Ind. Eng. Chem.*, 1914, 6, 577—580).—With the aid of the hydrogen electrode, the authors have developed an indicator method for the preparation of tri-

ammonium citrate solution. The hydron-concentration given by solutions of this salt, D 1'09, is shown to be  $10^{-7.4}$ . Rosolic acid is used as the indicator, and this concentration is obtained by the use of an easily prepared colour standard, made by mixing hydrochloric acid and disodium hydrogen phosphate solution. W. P. S.

**Estimation of the Phosphoric Acid of Basic Slag Soluble in Citric Acid.** F. HAUSSDING (*Landw. Jahrb.*, 1913, 45, 119—126).—Whilst the direct precipitation method and Lorenz' method gave the same results with pure solutions of ammonium phosphate, the latter method gave somewhat lower results when employed with basic slags; in the case of an abnormal slag the difference was as much as 0.58%. Popp's iron citrate method might take the place of the more elaborate method of the "Verband." It is considered, however, that Lorenz' method furnishes more correct results.

N. H. J. M.

**Estimation of Carbon in Soils and Soil Extracts.** J. W. AMES and E. W. GAITHER (*J. Ind. Eng. Chem.*, 1914, 6, 561—564. Compare T., 1906, 89, 595).—The carbon present in soils is oxidised completely, and carbonates are decomposed when from 1 to 3 grams of the soil are boiled for thirty minutes with a mixture consisting of 3.3 grams of chromic acid, 10 c.c. of water, and 50 c.c. of sulphuric acid (D 1.84), provided that the soil has been ground to pass through a 60-mesh sieve. If more water is added, the results obtained are too low. Carbon may also be estimated in 1% hydrochloric acid extracts of soils and in 4% ammonia solutions of humus by means of the chromic acid and sulphuric acid mixture. The alkaline permanganate method of oxidising the carbon was found to give low results.

W. P. S.

**Analysis of Illuminating Gas by the Bunte Burette, especially the Estimation of Carbon Monoxide.** E. CZABO (*Chem. Zentr.*, 1914, i, 1218; from *J. Gasbeleucht.*, 1914, 57, 169—172).—Carbon monoxide may be estimated accurately in gas by means of the Bunte burette provided that the gas is allowed to be in contact for two minutes with three successive quantities of 5 c.c. of colourless cuprous chloride solution; the gas should not be shaken with the solution. When it is desired to estimate hydrogen, methane, and nitrogen, in addition to carbon monoxide, the slow combustion method is to be preferred to the absorption process.

W. P. S.

**Condition of Carbonic Acid in the Blood. I. Method for the Estimation of Small Quantities of Carbonic Acid.** G. QUAGLIARIELLO and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 844—850).—The authors' experiments show that the sources of error in Winkler's method pointed out by Sørensen and Andersen (A., 1908, ii, 534) are negligible. They employ this method for the titration of carbonic acid, the carbon dioxide being extracted by a modification of Vesterberg's method (A., 1910, ii, 345), which

is described with a figure of the apparatus necessary, and by means of which the whole process can be carried out in the absence of air. The quantity of carbonic acid present in 1—10 c.c. of a 0.115*N*-sodium carbonate solution can be estimated with an error of 0.2—0.7%.

R. V. S.

**The Destruction of Organic Material by the Fresenius-Babo Method, after Preliminary Treatment with Antiformin, and the Estimation of Traces of Lead in Tissues Treated by this Method.** ALEXANDER FRIEDMANN (*Zeitsch. physiol. Chem.*, 1914, 92, 46—52).—The antiformin is prepared by treating bleaching powder with sodium carbonate, filtering off the precipitated chalk, and adding sodium hydroxide. The dried, powdered tissue is covered with a 50% antiformin solution, and allowed to remain for twenty-four hours. The particles become swollen, and are then readily attacked by the chlorate and hydrochloric acid employed in the Fresenius-Babo method.

The lead in the completely oxidised liquid is precipitated as sulphide, and subsequently estimated volumetrically by Kühn's method (A., 1906, ii, 493).

H. W. B.

**Analysis of Bronze and Brass.** RICHARD EDWIN LEE, JOHN P. TRICKEY, and WALTER H. FEGELEY (*J. Ind. Eng. Chem.*, 1914, 6, 556—560).—The following is an outline of the procedure recommended, the metals being estimated in separate portions of the alloy, with the exception of zinc, which is estimated in the filtrate from the iron if the latter is present. Lead is estimated as sulphate after the alloy has been dissolved in nitric acid in the presence of tartaric acid, whilst copper is estimated iodometrically by dissolving the alloy in nitric acid, adding potassium hydroxide solution, dissolving the cupric hydroxide in acetic acid, and adding potassium iodide. Tin and antimony are separated by treating the alloy with nitric acid, and weighed together, whilst another portion of the sample is dissolved in sulphuric acid and the solution titrated with permanganate solution in order to estimate the antimony. After heavy metals have been precipitated as sulphides, the zinc is titrated in the filtrate with ferrocyanide solution, iron, if present, having been removed previously by treating the oxidised filtrate with ammonia.

W. P. S.

**Investigation of Pyrophoric Cerium-Iron Alloys.** HANS ARNOLD (*Zeitsch. anal. Chem.*, 1914, 53, 496—503).—The method is as follows: 0.5—1 gram of the alloy is dissolved in hydrochloric acid containing bromine, about 0.5 gram of potassium chloride is added, and the silica rendered insoluble by evaporation. After collecting the silica, 3—5 grams of tartaric acid are added to the filtrate, and the solution is then poured into 50 c.c. of concentrated ammonia. After heating to 60° 15—30 c.c. of ammonium sulphide are added drop by drop while stirring. The precipitate, which besides the iron may contain also copper and zinc, is collected and washed with warm water containing ammonium sulphide and a

little ammonia, also some ammonium tartrate; it is then burnt to oxide and weighed, and then submitted to further analysis for copper and zinc, etc.

The filtrate from the iron is evaporated in a Kjeldahl flask, and the residue evaporated with 10 c.c. of concentrated nitric acid and 2 grams of potassium chlorate, which operation is then repeated with another 10 c.c. of acid and 1 gram of potassium chlorate; this completely destroys the tartaric acid. The residue is then dissolved in acid water, and the cerium precipitated as usual with oxalic acid. After destroying the excess of oxalic acid with nitric acid, etc., and removing traces of antimony with hydrogen sulphide any alumina is recovered by precipitation with ammonia.

L. DE K.

**Microchemical Detection of Aluminium and its Distribution in the Vegetable Kingdom.** ERNST KRATZMANN (*Chem. Zentr.*, 1914, i, 1459; from *Pharm. Post*, 1914, 47, 101—102, 109—113).—Characteristic crystals of caesium alum are obtained when a drop of a solution containing an aluminium salt is mixed on a microscope slide with a drop of a reagent consisting of equal volumes of a 2 mol. caesium chloride solution and an 8 mol. sulphuric acid solution. As little as 0.001 mg. of aluminium nitrate may be detected by the test. Plant ashes may be tested directly, but the addition of sulphuric acid is recommended when much calcium carbonate is present. The crystals are also obtained when sections of plants are treated with the reagent. Aluminium is of very frequent occurrence in plants, but the "alumina grains" mentioned by Radlkofer and Wehnert as being present in the leaves of *Symplocos* could be identified as aluminium compounds only in the case of *S. lanceolata* and *S. polystachya*.

W. P. S.

**Colorimetric Estimation of Small Quantities of Manganese in Water.** H. LÜHRIG (*Chem. Zeit.*, 1914, 38, 781—783. Compare (this vol., ii, 492).—Quantities of manganese amounting to less than 1 mg. per litre may be estimated accurately by treating 100 c.c. of the water with 3 c.c. of nitric acid (D 1.40) and an amount of silver nitrate more than sufficient to precipitate the chlorides present, then adding 3 grams of ammonium persulphate, and boiling the mixture for five minutes. The permanganate coloration obtained is compared with that shown by a known quantity of permanganate.

W. P. S.

**New Method of Separating Iron from Manganese.** O. HACKL (*Chem. Zentr.*, 1914, i, 1375; from *Jahrb. K. K. Geol. Reichsanstalt*, 1914, 63, 151—170).—When a neutral solution containing ferrous sulphate and manganese sulphate is boiled with the addition of potassium chlorate and zinc oxide, the iron is precipitated as basic ferric sulphate whilst the manganese remains in solution. At least 2.5 grams of potassium chlorate and 1.3 grams of zinc oxide are required for the precipitation of 0.2 gram of iron, and the volume of the solution should be 500 c.c. The basic ferric sulphate is collected on a filter, washed with cold water, and the quantity of iron then estimated volumetrically. The composition of the pre-

precipitate varies slightly according to the conditions of the precipitation.  
W. P. S.

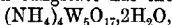
**The Analytical Examination of Tungsten.** HANS ARNOLD (*Zeitsch. anorg. Chem.*, 1914, 88, 74—87).—The methods adopted for the estimation of tungsten in ores are not suitable for the analysis of metallic tungsten. The finely powdered metal may be dissolved by a mixture of ammonia and hydrogen peroxide, or by ammonium persulphate. Coarser powders must be oxidised by alternately roasting and moistening with nitric acid. The massive metal is best dissolved electrolytically, using ammonia with a little ammonium persulphate in a platinum basin as cathode. Fragments of the metal also dissolve readily in fused potassium or sodium nitrite.

Strongly ignited tungsten trioxide is not attacked by ammonia, but if finely ground and mixed with a dilute solution of sodium carbonate, it is easily dissolved by ammonia. The ignited oxide is also dissolved if added in small quantities to hot ammonia solution.

In the analysis of tungsten an alkaline solution is mixed with tartaric acid (1 mol. to 1 mol.  $\text{WO}_3$ ), acidified with hydrochloric acid, and saturated with hydrogen sulphide whilst hot. The sulphide precipitate thus obtained is free from tungsten, but may contain some silica. Molybdenum and arsenic require special treatment in this group.

The separation of tungsten from the metals precipitated by ammonium sulphide is difficult. The benzidine precipitation (Knorre, A., 1905, ii, 286) is not quantitative. It is therefore necessary to precipitate tungstic acid by pouring the alkaline solution into boiling concentrated hydrochloric acid. The precipitate is washed with dilute acid. The filtrate contains the remaining metals, together with large quantities of alkali or ammonium salts, chiefly tartrate. It is evaporated to dryness and ignited in small quantities in a covered platinum basin. The carbon must not be completely removed, in order to prevent the oxidation of manganese.

Commercial ammonium tungstate has the formula

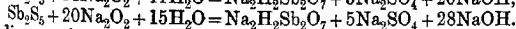


differing from the formula usually given, but corresponding with Werner's sodium paratungstate,  $\text{Na}_4\text{W}_5\text{O}_{17}\cdot 11\text{H}_2\text{O}$ . The minute quantities of impurities in several commercial varieties are tabulated.

C. H. D.

#### Detection of Antimony in Qualitative Inorganic Analysis.

JULIUS PETERSEN (*Zeitsch. anorg. Chem.*, 1914, 88, 108).—When antimony sulphide is warmed with water and sodium peroxide, the following reactions take place:



Sodium antimonate crystallises on cooling.

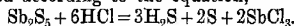
This reaction may be applied to the mixed precipitate containing sulphides of arsenic, antimony, and tin. When much tin is present, stannic oxide is precipitated, but may be removed by

filtering the boiling solution. Arsenic may be tested for after removal of antimony.  
C. H. D.

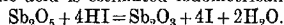
**Estimation of Antimony in Minerals.** A. CAFFIN (*Mon. Sci.*, 1914, [v], 4, i, 148—149).—Two methods are commonly used. The antimony sulphide isolated in the usual manner is weighed, and the sulphur contained therein estimated by conversion into sulphate in alkaline solution by means of a current of chlorine. After acidifying with hydrochloric acid and adding also some tartaric acid, the sulphate is decomposed with barium chloride, etc. This method, although tedious, is accurate, but, according to the author, it is necessary to free the ignited barium sulphate from any carbonate (due to co-precipitated barium tartrate) by treating with weak hydrochloric acid.

On the other hand, the process based on the electrolytic deposition of the antimony from its solution in sodium monosulphide (with addition of a little potassium cyanide or sodium sulphite) does not give, to judge from its appearance, a pure metallic deposit; in fact, the results are always too high, and the author suspects the presence of antimony hydride.  
L. DE K.

**Analysis of Stibium Sulphuratum Aurantiacum.** F. LUEHMANN and M. BERDAU (*Chem. Zentr.*, 1914, i, 1699—1700; from *Appt. Zeit.*, 1914, 29, 186—187).—The principle of the proposed method is as follows: Antimony pentasulphide is decomposed by concentrated hydrochloric acid according to the equation,



The antimony trichloride is then oxidised by hydrogen peroxide, and the antimonic acid is estimated iodometrically,



A quantity of about 0.2 gram of the substance is boiled with 25 c.c. of 25% hydrochloric acid until decomposed, 10 c.c. of hydrogen peroxide solution are added, the mixture is again boiled, and filtered through glass-wool. The cold filtrate is treated with 2 grams of potassium iodide, and the liberated iodine is titrated with thio-sulphate solution. Each c.c. of *N*/10-thiosulphate solution corresponds with 0.006 gram of antimony or 0.01 gram of antimony trioxide.  
W. P. S.

**Detection of Platinum with Stannous Chloride.** Egon LANGSTEIN and PAUL H. PRAUSNITZ (*Chem. Zeit.*, 1914, 38, 802).—In using the colour reaction described by Wöhler (*A.*, 1909, ii, 245) care should be taken that the solution to be tested for platinum does not contain organic substances, since these, when treated with *aqua regia* and hydrochloric acid, yield solutions giving a similar coloration to that yielded by platinum; for instance, filter-paper or the humus substances present in ores gives a coloration, under the conditions of the test, which may be mistaken for the platinum reaction. The test is trustworthy when organic substances present have been destroyed previously.  
W. P. S.

**Estimation of Small Quantities of Methane in Mine Gases.**

ERNST MURMANN (*Chem. Zentr.*, 1914, i, 1776; from *Österr. Chem. Zeit.*, 1914, 17, 69).—When the quantity of methane in a mine gas is less than 0.05% by vol., errors in its estimation may arise owing to the incomplete absorption of the carbon dioxide. This may be remedied by causing the inlet tubes to the absorption vessels to dip into the barium hydroxide solution; the end of the inlet tubes should also be drawn out into fine jets. With these alterations no trace of carbon dioxide will be found in the third absorption vessel.

W. P. S.

**Separation of Hydrocarbons by Liquid Sulphur Dioxide.**

L. EDELEANU (*Chem. Zentr.*, 1914, i, 1785; from *Petroleum*, 1914, 9, 862—864).—Aromatic and cyclic unsaturated hydrocarbons may be estimated in petroleum distillates by shaking the latter with liquid sulphur dioxide; these hydrocarbons are soluble in the sulphur dioxide, whilst the paraffin and naphthene hydrocarbons are practically insoluble. The estimation is carried out at a temperature of  $-12^{\circ}$ , and a thick-walled graduated burette is employed.

W. P. S.

**Spindle Pyknometer, a New Instrument for the Estimation of Alcohol.**

H. WÜSTENFELD and CH. FOEHR (*Chem. Zentr.*, 1914, i, 1537; from *Deut. Essigind.*, 18, 114—116, 125—127).—The use of the ordinary form of pyknometer in the estimation of alcohol is hampered by imperfect meniscus formation. To overcome this defect, Klemann has devised an apparatus which, when filled with the distillate, floats in toluene. The construction is obvious from the figure. The liquid to be investigated is poured into *a* and the height read off on the scale *b*. *c* is a glass bulb which increases the buoyancy of the apparatus. The level of filling and the floating equilibrium are determined from the graduated scale. The volume of the liquid in the spindle is determined by weighing with distilled water, the weight by immersion in toluene. The apparatus has the advantage over the weight pyknometer that determinations can be made without using the balance. Only 50 c.c. of distillate are required. The contents need not be brought to a definite mark or to normal temperature if temperature-correction tables are used. One instrument suffices for solutions containing 0—12% of alcohol. The density of toluene at different temperatures (compared with water at  $15^{\circ}$ ) has been determined:  $12.5^{\circ}$ , 0.87228;  $15^{\circ}$ , 0.87005;  $17.5^{\circ}$ , 0.86774 (0.86773);  $20.0^{\circ}$ , 0.86550 (0.86543);  $22.5^{\circ}$ , 0.86314;  $25.0^{\circ}$ , 0.86089.



H. W.

**A Colour Reaction given by Quinol in the Solid State.**

MAUDINEY (*Compt. rend.*, 1914, 158, 1782—1783).—On mixing together a little solid potassium carbonate and quinol a pale blue



coloration is obtained, which gradually deepens in intensity to that of Prussian blue. This colour is destroyed by water, alcohol, or ammonia, slowly by ether, and immediately by heat. Chloroform and benzene are without effect on it. The solution in water is yellow, gradually turning brown, the liquid on evaporation yielding brown crystals. The blue substance becomes brownish-black in a few hours on exposure to air. With sodium carbonate quinal gives a mauve-grey coloration, and with ammonium or lithium carbonates no coloration.

W. G.

**Influence of Atmospheric Conditions in the Testing of Sugars.** F. J. BATES and F. P. PHELPS (*J. Washington Acad. Sci.*, 1914, 4, 317—318\*).—Experiments have been made to determine the correction for the loss of water by evaporation during the filtration of raw sugar solutions under varying atmospheric conditions. The observations are satisfactorily represented by the equation  $Q = CT(P_s - P_a)$ , where  $Q$  is the change due to evaporation in time  $T$ ,  $P_s$  the vapour pressure of the sugar solution, and  $P_a$  the pressure of the water vapour in the atmosphere. If the solution is not poured back upon the filter, the change is so small as to be negligible in ordinary sugar testing. In this case the experiments gave  $C = 0.00017$ , whereas experiments in which the solution was returned to the filter gave  $C = 0.0006$ .

H. M. D.

**Estimation of Saccharine Substances in the Liver.** H. BIEREY and (Mme.) Z. GRUZEWSKA (*Compt. rend.*, 1914, 158, 1828—1830).—The total carbohydrate content of the liver is estimated as follows: Immediately after death the liver is removed, weighed, ground to pulp, and a portion (10—25 grams) weighed out and frozen with liquid air. The solid mass is ground up in a mortar, inserted in a freezing mixture, transferred to a flask with 100 c.c. of 5% hydrochloric acid, and heated in an autoclave at 120° for thirty minutes. The cold liquid is neutralised with sodium hydroxide, the protein substances precipitated with mercuric nitrate and filtered off, and the filtrate neutralised and made up to 300 c.c. In this solution the excess of mercury is eliminated by addition of zinc dust, and the sugar then estimated by the Mohr-Bertrand method. By this method and their method for estimating glycogen (compare A., 1913, ii, 160, 635) the authors have determined the amount of glycogen and total carbohydrate, both expressed as dextrose, in the livers of marmots at the end of winter, and in livers of dogs, rabbits, and chicken. In the case of the cold-blooded animal, the marmot, the glycogen and total carbohydrate content are practically equal, whereas in the case of the normal homothermic animals, the dog, rabbit, and chicken, there is always a small amount of carbohydrate in addition to the glycogen, which is present either as free sugar or as reserves other than glycogen.

W. G.

**Estimation of Sugars in Beet Molasses by Clerget's Method.** E. SAILLARD, WEHRUNG, and RUBY (*Chem. Zentr.*, 1914, i, 1781—1782; from *Mon. Sci.*, 1914, [v], 4, 232—245).—Since the ordinary Clerget

\* and *Zeitsch. Ver. Deut. Zuckerind.*, 1914, 579—586.

method yields low results, owing to the fact that the proteins in molasses exhibit a different rotation in alkaline and acid solutions, the following method is recommended for the estimation of sugars in beet molasses. Fifty-two grams of the molasses are treated with 20 c.c. of basic lead acetate solution, diluted to 200 c.c., and filtered; 100 c.c. of the filtrate are then treated with sulphur dioxide or oxalic acid to remove lead, the acid is neutralised with calcium carbonate or barium carbonate, a small quantity of animal charcoal is added, and the mixture is filtered. Fifty c.c. of the filtrate are then mixed with a quantity of sodium chloride equivalent to the amount of hydrochloric acid used for the subsequent inversion, the solution is diluted to 100 c.c., and polarised at  $20^{\circ}$  (reading= $A$ ). Another quantity of 50 c.c. of this filtrate is then mixed with 25 c.c. of water and 6.5 c.c. of hydrochloric acid (D 1.18), inverted, neutralised with sodium hydroxide, cooled to  $20^{\circ}$ , diluted to 100 c.c., and polarised (reading= $B$ ). The percentage of sugar,  $S$ , is calculated from the formula:

$$S = \frac{200(A+B)}{\text{Coeff. of inversion} - t/2}$$

(compare A., 1912, ii, 698).

W. P. S.

**Estimation of Mannitol.** JAN SMIT (*Zeitsch. anal. Chem.*, 1914, 53, 473—490).—The processes based on the crystallisation of the mannitol, its polarimetric determination in presence of borax, and on its power of forming additive products with aldehydes are unsuitable in practice.

The process employed by Wagenaar for the estimation of glycerol (A., 1911, ii, 663) (which depends on the titration of copper hydroxide held in solution in presence of free alkali) has, however, been found useful for the estimation of mannitol. Of course, a special table had to be constructed, and interfering substances should be absent. Ammonia and also dextrose may be eliminated by heating with sodium or calcium hydroxides; sugar may also be got rid of by fermentation. Colouring matters formed may be removed by basic lead acetate, the excess of which is then in turn removed by sulphuric acid, and any lactic acid present is extracted with ether. Glycerol may be removed previously from the dry residue by extracting with a mixture of two volumes of absolute alcohol, and three volumes of ether. Amino-acids may be removed with phosphotungstic acid. Sorbitol and dulcitol, which, however, occur but rarely, interfere with the direct application of the process.

L. DE K.

**Estimation of Rhamnose in the Presence of Other Methylpentoses.** EMIL VOROČEK and R. POTNĚŠIL (*Bull. Soc. chim.*, 1914, [iv], 15, 634—639).—Rhamnose can be estimated in presence of other methylpentoses by conversion into the corresponding nitrile, hydrolysis to  $\alpha$ -rhamnohexonic acid, and oxidation of this substance to mucic acid by the action of nitric acid. When other methylpentoses, such as rhodose, are present, the total amount of these sugars can be determined by the methylfurfuraldehyde

method, the percentage amount of those other than rhamnose being estimated by difference.

A. J. W.

**Estimation of Glycogen in Yeast.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1914, 92, 75-88).—A critical examination of Euler's method (this vol., i, 635) for the estimation of glycogen in yeast. Experiments by the present author show that yeast "gum" is not destroyed by the boiling alkali employed in Euler's process, and, therefore, as it also furnishes dextrose on hydrolysis, a portion of what is assumed by Euler to be glycogen is, in reality, yeast "gum." Further experiments lead the author to conclude that, owing to the presence of other substances of a cellulose-carbohydrate nature, it is impossible separately to estimate the glycogen in yeast.

H. W. B.

**Estimation of Hydrocyanic Acid and Alkali Cyanides.** G. E. F. LUNDELL and J. A. BRIDGMAN (*J. Ind. Eng. Chem.*, 1914, 6, 554-556).—The method described consists in rendering the cyanide solution slightly ammoniacal, adding a small quantity of dimethylglyoxime solution, and titrating the mixture with a standardised nickel ammonium sulphate solution; the dimethylglyoxime serves as the indicator, since no permanent red precipitate of nickel dimethylglyoxime is obtained until all the cyanide has been combined, according to the equation  $\text{NiSO}_4 + 4\text{KCN} = \text{K}_2\text{Ni}(\text{CN})_4 + \text{K}_2\text{SO}_4$ .

W. P. S.

**The Insoluble Bromide Number of Oils and its Estimation.** ALEX. GEMMELL (*Analyst*, 1914, 39, 297-308).—Since the results obtained in the estimation of the insoluble bromide number of oils are influenced by various conditions of experiment, and particularly by the solubility factor, the following method of procedure is recommended as being capable of yielding trustworthy and concordant results. Five grams of the oil are saponified with alcoholic potassium hydroxide solution, the soap is dried, dissolved in 100 c.c. of water, and the fatty acids are liberated. After cooling, 30 c.c. of ether are added, the ethereal layer is separated, the aqueous portion is shaken with 20 c.c. of ether, and the whole ethereal extract is diluted with ether to 100 c.c. Twenty c.c. of this solution are then treated with 2 c.c. of glacial acetic acid, cooled in ice-water, and bromine is added. The precipitate is washed five times with cold ether, using 5 c.c. each time, then dried and weighed. It is better to work with the fatty acids, as secondary reactions take place when the glycerides are brominated directly. The precipitates obtained from the fatty acids approximate more closely in composition to the pure hexabromide (vegetable oils) or octabromide (marine animal oils) than is the case when the glycerides themselves are employed for the estimation.

W. P. S.

**A New Reaction of Fats (Chromium-chrysoidine Reaction). Fatty Substances of the Epidermal Tissue in General.** LEONARDO MARTINOTTI (*Zeitsch. physiol. Chem.*, 1914, 91, 425-439).—A group of dyes belonging to the class of aminoazo-compounds

have the property of fixing fats, and, in the presence of an oxidising reagent, of making them insoluble. Chrysoidine lends itself well to this purpose, and the best oxidisers are chromic acid and the dichromates. All these substances stimulate the formation of epithelium in skin wounds. The reaction demonstrates the presence of fatty substances in the human epidermis, especially in the membranes, in keratohyalin, eleidin, and the eleidin derivatives of nail and hair.

In staining by this method, the material is fixed in 10% formaldehyde, cut by the freezing microtome, and immersed for five to ten minutes or longer in a 1% aqueous chrysoidine solution. After washing for a short time, the sections are placed in the oxidising agent (10% chromic acid or potassium dichromate) for one minute, then washed and mounted in the usual way. Detailed recommendations are made as to the choice of particular dyes and oxidising agents in the groups mentioned in order to obtain the best results with different tissues.

R. V. S.

**The Melting and Solidifying Points of Mixtures of Fatty Acids and the Use of these Points to Estimate the Composition of such Mixtures.** E. TWITCHELL (*J. Ind. Eng. Chem.*, 1914, 6, 564—569).—Whilst the lowering of the solidifying point of a pure, fatty acid caused by the addition of other fatty acids varies too much to permit the use of this method in calculating the composition of a mixture of fatty acids, the lowering of the melting point is more constant. The author has applied the melting-point method to the solid fatty acids obtained from various oils and hydrogenated oils, and gives the results of the investigation in detail. The fatty acids of cottonseed oil were found to consist of palmitic acid, 25.9%, and unsaturated acids with eighteen carbon atoms, 72.8%. The fatty acids of menhaden oil contained palmitic acid, 22.7; other solid, saturated acids, 11.8; unsaturated acids with eighteen carbon atoms, 26.7; and unsaturated acids with twenty-two carbon atoms, 20.2%.

W. P. S.

**The Estimation of  $\beta$ -Hydroxybutyric Acid.** ERNEST LAURENCE KENNAWAY (*Biochem. J.*, 1914, 8, 230—245).—A full description of work of which a preliminary account has already been given (this vol., ii, 304).

H. W. B.

**Estimation of Lactic Acid.** CHARLES G. L. WOLF (*J. Physiol.*, 1914, 48, 341—347).—It is found that the estimation of lactic acid by means of the zinc salt gives more satisfactory results than by the oxidation methods. In concentrating the fluids containing the acids, the evaporation should take place in a vacuum at as low a temperature as possible, to avoid loss of the acid. The extraction from the concentrated solution by ether is best accomplished by absorbing the solution on blotting paper (Adams' paper), and extracting in a Soxhlet apparatus for three to four hours. The proteins may be removed in a quite satisfactory manner by Schenk's reagent.

S. B. S.

**Detection of Malonic Acid.** H. J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1914, 17, 477).—The substance under examination is mixed with anhydrous methyl or ethyl alcohol containing hydrochloric acid, the mixture is heated for a few minutes, then neutralised, and an alcoholic solution of bromomethylfurfuraldehyde is added. On rendering the mixture slightly alkaline with alcoholic potassium hydroxide solution, an intense blue fluorescence is obtained if malonic acid or its esters are present. The reaction appears to be characteristic of these substances, and is not given by acetoacetic and dicarboxyglutaconic esters. W. P. S.

**Examination of Iron Gallate Inks.** Apparatus for the Extraction of these Inks with Ethyl Acetate. RICHARD KEMPF (*Chem. Zentr.*, 1914, i, 1531; from *Mitt. K. Materialprüfungs.-Amt, Gross Lichterfeld*, 1914, 31, 451—455).—The apparatus consists of a tall glass vessel provided with a cooling jacket; the spiral stem of a funnel extends to the bottom of the vessel, and the lower end of the stem ends in a bulb having fine perforations. The condensed solvent (ethyl acetate) from the reflux apparatus falls into the funnel, passes down the stem, and rises in the form of small drops through the acidified ink contained in the vessel; the solvent collects on the surface of the ink, and flows thence back into the extraction flask. W. P. S.

**Estimation of the Oxyproteic Acid Fraction in Normal and Pathological Urines.** REMPEL SASSA (*Biochem. Zeitsch.*, 1914, 64, 195—221).—The author has subjected to a critical experimental examination the various methods for estimating the "oxyproteic" fraction of urines (that is, the acids yielding barium salts soluble in water, but insoluble in mixtures of ether and alcohol, and giving a precipitate with mercuric acetate). He has devised a modified method, the essential point of which is that the liquid containing the soluble barium salts is evaporated to a syrup and then mixed with kieselguhr before extraction with the mixture of alcohol and ether. The "oxyproteic" nitrogen was found to vary very little in normal individuals (4.3—4.7% of the total nitrogen), whereas in cases of cachexia, including carcinomatous and phthisical patients, it was markedly increased (5—9.6%). This increase is not, however, distinctive of carcinoma, as other authors have stated. S. B. S.

**The Analysis of Essential Oils.** A. BÉHAL (*Bull. Soc. chim.*, 1914, [iv], 15, 565—568).—An examination of the cause of error in the estimation of esters in essential oils by the usual method. The author finds that it is due to the formation of small amounts of ethyl esters on heating the oils with  $N/2$ -alcoholic potassium hydroxide. These ethyl esters, being volatile, are not condensed in the apparatus usually employed. The author has determined the loss in the case of a number of pure acetic and formic esters commonly occurring in essential oils. The loss is greater the longer is the time of contact and the smaller is the amount of

alkali used. The error can be largely eliminated by using a water reflux condenser, or, better, by working in a sealed tube at 100°.

W. G.

**Detection of Acetone in Urine.** FLEISCHMANN (*Chem. Zentr.*, 1914, i, 1784; from *Schweiz. Apoth. Zeit.*, 1914, 52, 222).—Ten c.c. of the urine are mixed in a test-tube with 1 c.c. of acetic acid and four drops of a 5% sodium nitroprusside solution; 10 c.c. of ammonia are then poured on the surface of the mixture. When acetone is present, a violet-coloured ring appears at the junction of the two liquids. Alcohol and aldehyde do not give the reaction.

W. P. S.

**Turbidity Methods for the Determination of Acetone, Acetoacetic Acid, and  $\beta$ -Hydroxybutyric Acid in Urine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 18, 263—271).—The relative turbidities of the unknown and standard solutions, after treatment with certain reagents, are measured by means of an ordinary Duboscq colorimeter, in the same way as are ordinary colour intensities.

The acetone in from 0.5 to 5 c.c. of urine is first transferred by a rapid air current into 10 c.c. of a 2% solution of sodium hydrogen sulphite, then diluted and mixed with 15 c.c. of Scott-Wilson's mercury cyanide reagent. After bringing to 100 c.c., the turbidity is compared with a similar solution prepared from a known quantity of acetone. The acetoacetic acid + acetone is similarly estimated by heating the urine during the aspiration, which converts the whole of the acid into acetone.

For the determination of  $\beta$ -hydroxybutyric acid, the urine is first boiled to expel acetone and acetoacetic acid, and then distilled with potassium dichromate and sulphuric acid, as in Shaffer's method. The acetone thus formed is then estimated by the turbidity produced by the Scott-Wilson reagent, as already indicated above. The accuracy is such that when various quantities of  $\beta$ -hydroxybutyric acid were added to urine, the quantities actually found by this method in seventeen instances were within 97 to 101% of the theory.

H. W. B.

**A Manometric Method for the Estimation of Urea (Carbamide).** WALTHER LÖB and ARTUR PROROK (*Biochem. Zeitsch.*, 1914, 65, 273—282).—The substance containing carbamide is allowed to flow into the hypobromite solution from a graduated cylinder. Both the cylinder and vessel containing the hypobromite reagent are connected with a manometer, and the whole apparatus (which consists of glass and is figured in the text) can be immersed in a thermostat. The manometer, when small quantities of carbamide only are to be estimated, can be filled with water instead of mercury. The apparatus can be calibrated with solutions of pure carbamide before use. To estimate carbamide in serum, 5—10 c.c. of this fluid will suffice when a water manometer is employed.

S. B. S.

**Creatine and Creatinine Metabolism. II. The Estimation of Creatine.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1914, 18, 191—194).—The procedure consists in evaporating the creatine solution, to which has been added about an equal bulk of normal hydrochloric acid, to dryness. This quantitatively converts amounts of creatine up to 100 milligrams into creatinine, which is then estimated colorimetrically by Folin's method. When applied to urine, a pinch or two of powdered or granulated lead must also be added to prevent the formation of pigment. The production of any turbidity in the subsequent process of estimation due to the presence of traces of dissolved lead is prevented by the addition of 5% Rochelle salt to the alkali solution employed. This process is claimed to be accurate and very rapid. H. W. B.

**Berberine and its Estimation.** EAW. RICHTER (*Arch. Pharm.*, 1914, 252, 192—205).—Picrolonic acid is a very suitable reagent for the gravimetric estimation of berberine in its salts and drugs (compare Matthes and Rammstedt, A., 1907, ii, 592). Its suitability was first tested by means of berberine chloride, the purity of which was indicated by an estimation of the water (by drying in a vacuum; compare Frerichs and Stoepel, A., 1913, i, 1094) and chlorine (found, 12.65 and 8.22% respectively). A solution of the chloride (about 0.1 gram) in 20 c.c. of water is treated in a separating funnel with 10 c.c. of 15% sodium hydroxide, and then with 60 grams of ether. After the base has dissolved completely in the ether, 40 grams of the ethereal solution are treated with 5 c.c. of approximately *N*/10-picrolonic acid, the mixture is shaken for a short time, and after about an hour the precipitated picrolonate is collected in a Gooch crucible, washed with 10 c.c. of a mixture of alcohol and ether (3:1), and dried at 110°. The percentage of berberine found is 79.32 ( $C_{29}H_{18}O_4NCl \cdot 3H_2O$  requires berberine 78.97, water 12.69, and Cl 8.34%).

Berberine in a drug or tincture is estimated as follows. The coarsely powdered drug, 2.5 grams, is completely extracted by alcohol in a Soxhlet apparatus. The alcoholic extract is freed from alcohol on the water-bath, the residue is dissolved in 15 c.c. of water, 10 c.c. of 15% sodium hydroxide and, after shaking, 60 grams of ether are added; the mixture is shaken for fifteen minutes, 1 gram of tragacanth powder is added, and the mixture is shaken until the liquid is quite clear. Twenty-four grams of the yellow ethereal solution (equivalent to 1 gram of the drug) are treated with 5 c.c. of approximately *N*/10-picrolonic acid, and the resulting precipitate is collected and treated as above. The weight multiplied by 56.1 gives the percentage of berberine in the drug.

The estimation of the berberine in a tincture is very similar to the preceding. C. S.

**Microchemical Detection of Strychnine and Brucine in the Seeds of *Strychnos Nux Vomica*.** R. WASICKY (*Chem. Zentr.*, 1914, i, 1464; from *Zeitsch. Allg. Österr. Apoth. Ver.*, 1914, 52, 35, 41—42, 53—55, 67—69).—Investigation of many proposed

tests showed that inorganic reagents are usually of little use in the detection of brucine and strychnine in vegetable preparations. Mayer's and Marne's reagents react only with strychnine, whilst iodine-potassium iodide gives mixed crystals of both alkaloids. Gold chloride gives a reaction which to some extent distinguishes the alkaloids from one another, and potassium ferrocyanide serves for the detection of strychnine. Picrolonic acid is the best reagent for the detection of brucine in the presence of strychnine; with strychnine it yields small, needle-shaped yellow crystals, which do not change when heated, whilst with brucine it gives a flocculent precipitate, which on warming forms clusters of rhombic, optically active crystals.

W. P. S.

**Estimation of Albumin in Urine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1914, 18, 273—276).—Two methods are described. The "turbidity" method consists in comparing the turbidities produced by sulphosalicylic acid in the unknown and standard protein solutions, and the gravimetric method in coagulating the protein in 10 c.c. of the urine contained in a weighed centrifuge tube, washing with water and alcohol, and drying at 100° to constant weight. Both methods give approximately the same results.

H. W. B.

**Detection of Albumin and Other Proteins in Urine. Reactions of an Acetic Acid Soluble Albumin.** A. LESPINASSE (*Chem. Zentr.*, 1914, i, 1710; from *Bull. Sci. Pharmacol.*, 1914, 21, 150—156).—The presence of albumin in the urine of persons who daily take doses of quinine can only be detected by the coagulation test after the urine has been rendered slightly acid with acetic acid and treated with a small quantity of sodium chloride; the usual precipitating reagents cannot be used with such urines. Protein decomposition products may be detected in the filtrate from the albumin precipitate by means of the biuret reaction. In certain urines the author noted the presence of an albumin which was soluble in acetic acid; this albumin was precipitated by dilute acetic acid, but dissolved readily in an excess of the acid, and was not reprecipitated by nitric acid. Hot hydrochloric acid precipitated the albumin, but the precipitate dissolved in an excess of the acid, yielding a violet-coloured solution. Millon's, Tanret's, and Esbach's reagents yielded precipitates with the urine. The precipitate obtained by heating the urine with a small quantity of acetic acid did not dissolve when the mixture was boiled for twenty minutes, but when an excess of the acid was added before boiling, no precipitate was obtained. All the proteins present were precipitated on heating the urine with trichloroacetic acid, and the filtrate gave no reaction with the biuret test.

W. P. S.

**Precipitation of Lactalbumin in Cows' Milk.** W. O. WALKER and A. F. GRANT CADENHEAD (*J. Ind. Eng. Chem.*, 1914, 6, 573—574).—The following method yields more trustworthy results than does that in which the albumin is separated by heating the filtrate from the casein precipitate with acetic acid. After the casein has been



precipitated with dilute acetic acid and removed by filtration, the filtrate is neutralised with sodium hydroxide solution, one drop of 10% acetic acid is added, the solution heated to 45° and treated with a reagent consisting of 8 grams of tannin, 190 c.c. of 50% alcohol, and 8 c.c. of 25% acetic acid. The precipitate is collected after thirty minutes, and the nitrogen estimated in it by Kjeldahl's method, the factor 6.34 being used to calculate the nitrogen into albumin.

W. P. S.

**Estimation of Casein in Milk by means of the Tetraserum.** B. PRYL and R. TURNAU (*Arb. K. Gesundheitsamte.*, 1914, 47, 347—361).—The following volumetric method is proposed: 50 c.c. of the milk are treated with six drops of 1% phenolphthalein solution and titrated with  $N/10$ -alkali solution. A second quantity of 50 c.c. of the milk is then mixed in a stoppered flask with 5 c.c. of carbon tetrachloride and 1 c.c. of 20% acetic acid (the acidity of this acid must be estimated accurately), the mixture is shaken thoroughly, and filtered; 25 c.c. of the filtrate (tetraserum) are now titrated with  $N/10$ -alkali solution. From the first titration and the acidity of the acetic acid is calculated the quantity of alkali used for 25 c.c. of milk plus 0.5 c.c. of acetic acid ( $a$  c.c. of  $N/10$ -alkali solution); then, knowing the quantity of alkali solution used for the titration of the serum ( $b$  c.c. of  $N/10$ -alkali solution) and the amount of fat in the milk ( $f$  grams per 100 c.c.), the quantity of casein (grams per 100 c.c.) is calculated from the formula  $x = 0.457(a - b.99.3 - f/100)$ . By taking into account the specific gravities of the milk and the serum, slightly more accurate results may be obtained. The authors find that casein obtained from milk contains 15.5% of nitrogen, and that each gram of the protein requires 8.75 c.c. of  $N/10$ -alkali solution for neutralisation towards phenolphthalein.

W. P. S.

**A Titration Method for the Estimation of Phytin.** WOLFGANG HEUENEER and HERMANN STADLER (*Biochem. Zeitsch.*, 1914, 64, 422—437).—Phytic acid in presence of 0.6% hydrochloric acid can be estimated by titration with ferric chloride solution containing 0.05 to 0.2% of the iron salt and 0.6% hydrochloric acid, ammonium thiocyanate in 0.03% concentration (of initial volume) being employed as indicator. One mg. of iron corresponds with 1.19 mg. of phytin. The titration can be carried out in the presence of inorganic phosphates or esters of phosphoric acid, which are not precipitated in the presence of acid, provided that they are not present in too large excess over the phytin.

S. B. S.

**Method of Increasing the Sensitiveness of Telmon's Reaction for the Detection of Blood in Organic Liquids.** GEORGES ROBILLON (*Chem. Zentr.*, 1914, i, 1706; from *Bull. Sci. Pharmacol.*, 1914, 21, 156—157).—This test may be rendered about one hundred times more sensitive by mixing 10 c.c. of the liquid under examination with 2 c.c. of Meyer's reagent (this must be quite colourless) and a few drops of hydrogen peroxide; from 2 to 3 c.c.

of 90% alcohol are then poured on the surface of the mixture. A red coloration appears at the junction of the two liquids if blood is present. Urine containing pus, but free from blood, gives a positive reaction with the original test; if, however, such urine be diluted until it no longer gives a reaction, and then further diluted with ten times its volume of water, the presence or absence of blood may be ascertained by means of the modified test.

W. P. S.

**Sensitiveness of the Peroxydase Reaction.** A. BACH (*Ber.*, 1914, 47, 2122—2124).—The author has subjected the solution of peroxydase obtained from horse-radish to purification by means of ultra-filtration, for which process a simple but convenient apparatus is described. The product was much more active than that obtained by Bach and Tscherniak (*A.*, 1908, i, 746), and still more so than that described by Bach and Chodat (*A.*, 1903, i, 377). For testing the sensitiveness of the peroxydase reaction, guaiacol is found to be the most suitable substance, on account of its relative resistance to hydrogen peroxide in the absence of a catalyst. When a mixture of 8 c.c. of a 0.1% solution of guaiacol with 1 c.c. of a 0.1% solution of hydrogen peroxide was treated with 1 c.c. of a solution containing one part by weight of dry peroxydase per 10<sup>9</sup> parts of water, a brownish-red coloration is distinctly visible after twenty minutes, and gradually deepens. D. F. T.

**Nephelometry in the Study of Nucleases.** PHILIP ADOLPH KOREK and SARA S. GRAYES (*J. Amer. Chem. Soc.*, 1914, 36, 1304—1310).—A method is described for estimating undigested nucleic acids which consists in adding a 0.2% solution of egg-albumin, faintly acidified with acetic acid, to a dilute solution of the nucleic acid, and estimating the resulting suspensoids by means of the nephelometer. The reagent is not appreciably affected by most substances met with in physiological work, and will readily detect 1 part of yeast nucleic acid in 1,000,000 parts of water.

E. G.

**The Cammidge Pancreas Reaction.** C. A. PEKELHARING and C. J. C. VAN HOOGENHUYZE (*Zeitsch. physiol. Chem.*, 1914, 91, 151—164).—The authors' experiments indicate that this reaction (Cammidge, *British Med. Journal*, 1906, 1130) is due to animal gum or urinary dextrin present in small quantity in normal urine and in increased quantity in pathological cases, in which it is sufficient to give rise to Cammidge's reaction. This "dextrinuria" can be produced in normal persons by the administration of large quantities of sugar.

R. V. S.

**Applicability of the Dialysis Process to the Investigation of Clinical and Biological Questions.** EMIL ABDERHALDEN (*Chem. Zentr.*, 1914, i, 920; from *Munch. med. Woch.*, 1914, 61, 233—238).—Attention is called to the various sources of error, especially as regards the dialysing membranes, as there is no material known

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which is permeable to peptones but not to proteins. The proteins can also be separated by coagulation, and experiments are being made to apply the method of ultra-filtration. Another source of error is that the substrate may yield non-specific reactions. The author describes a dialysis apparatus which he uses in his experiments.

S. B. S.

**Adsorption Phenomena in Abderhalden's Dialysis Process.** F. PLAUT (*Chem. Zentr.*, 1914, i, 920; from *Munch. med. Woch.*, 1914, 61, 238—241).—An increase of substances which can yield a positive ninhydrin reaction in the dialysate can be caused by the presence of inorganic substances like kaolin, barium sulphate, talc, and kieselguhr. It is possible that organic substances such as are used in Abderhalden's reaction have a similar effect. Such phenomena as these described may lead to erroneous results in the applications of the reactions.

S. B. S.

**The Abderhalden Reaction.** HELMUTH THAR, and NINA KORNCHNEV (*Biochem. Zeitsch.*, 1914, 63, 483—496).—The authors have directed their experiments to ascertain whether the serum of pregnant individuals really produces a degradation of the placenta proteins in accordance with Abderhalden's theory of protective ferments. They carried out a large number of experiments by means of the dialysis method, and collected together a portion of the dialysates of both sera alone (of pregnant and normal individuals) and of sera with placenta. In the collected dialysates from a large number of tests, the total and amino-nitrogen (by van Slyke's method) were estimated. In the non-pregnant cases the dialysates from the serum alone did not contain more total nitrogen and amino-nitrogen than the dialysates of sera + placenta. On the other hand, in the pregnant cases (of which the dialysates yielded a positive ninhydrin reaction, but negative reactions with the biuret and sulphosalicylic acid tests), the dialysates from the serum + placenta dialysates contained more total and amino-nitrogen than the dialysates from serum alone. This increase was not observed when the dialysis was carried out at 0°. On the other hand, experiments by the optical method, and by the estimation of amino-nitrogen when sera were allowed to act on placenta peptone, failed to reveal any difference between the actions of sera from pregnant and normal cases. The evidence that the pregnant sera contain a ferment which breaks down placenta proteins is insufficient.

S. B. S.

